SYNTHESIS AND PERFORMANCE OF GRANULATED BLAST FURNACE SLAG (GBFS) BASED GEOPOLYMERS ON COPPER REMOVAL FROM AQUEOUS SOLUTION

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CHEMICAL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

SEPTEMBER 2015

Synthesis and Performance of Granulated Blast Furnace Slag (GBFS) Based Geopolymers on Copper Removal from Aqueous Solution

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Prof Dr Khairun Azizi Mohd Azizli)

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September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NURFARAHIN BINTI BURHANUDDIN

ABSTRACT

The presence of large quantities of heavy metals such as copper in the industrial waste water poses harms to the human health and environment. This has become a concern and industry are searching for low cost adsorbents to treat and remove heavy metals from waste water. Past studies have shown the potential of geopolymers as potential adsorbent due to its amorphous and porous structure. In this study, geopolymers from granulated blast furnace slag (GBFS) were synthesized. The geopolymers were synthesized with a mixed designs of different silica ratio of alkaline activator. It was found that different silica ratio of alkaline activator created a different form of geopolymer. The optimum ratio is chose based on the porosity volume. Another study is done by modifying the GBFS based geopolymer with pore forming agent; poly ethylene glycol (PEG) and hydrogen peroxide (H_2O_2) which improved the copper removal. GBFS based geopolymers, PEG incorporated geopolymer and H_2O_2 incorporated geopolymer synthesized were characterized for porosity and surface area, surface images, particle size and thermal stability before being utilized for batch adsorption test of copper. Batch adsorption tests were conducted on copper sulphate solution and the adsorbent dosage, contact time and pH were varied. The optimum silica ratio of the GBFS based geopolymer was the GP-0.75. Meanwhile, the amount of PEG and H_2O_2 added were based on previous researches; 3% of PEG to PEG incorporated geopolymer and 8% of H_2O_2 to H_2O_2 incorporated geopolymer. The percent removal of copper for GBFS based geopolymer was only up to 70% while geopolymers with pore forming agent could achieve up to 80%. The adsorption activities for GP-0.75 fitted pseudo second order kinetic models while for GP-0.75 PEG and GP-0.75 H_2O_2 fitted the pseudo first order kinetic model. So forth, GP-0.75 fitted well in Freundlich isotherm while GP-0.75 PEG and GP-0.75 H_2O_2 fitted well in Langmuir isotherm for the isotherm equilibrium study.

ACKNOWLEDGEMENT

The writer of this report is a Chemical Engineering student from Universiti Teknologi PETRONAS (UTP). This final year report title is 'Synthesis and performance of granulated blast furnace slag (GBFS) based geopolymers on copper removal from aqueous solution'.

The author would like to extend her gratitude to Allah the Almighty God because of His will, the author managed to complete this final year project on time.

The author also would like to thank her supervisor Prof. Dr. Khairun Azizi Mohd Azizli, for her dedication, support and enthusiasm in guiding author to complete her work on time. She has been helping author to coordinate the project especially in writing this report. She has been assisting whenever there are any difficulties at any parts with patience and kindness through the entire project.

Not forgetting, thanks to the post graduate student Muhammad Irfan Khan for serving as a mentor to help the author in research development.

A special gratitude also is expressed to author family members and friends. The successful completion of this project would not have been possible without their guide and supports. The gratitude also extends to all Universiti Teknologi PETRONAS staffs especially the laboratory technician and assistance for their commitment and supports.

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1.1 Background of Study

1.1.1 Introduction to GBFS

Blast furnace slag is a waste product in the iron production which has two basic types; blast furnace slag-granulated (amorphous) and non-granulated (crystalline). It is formed when iron ore or pellets, coke and a flux are melted together in a blast furnace. When the process is complete, the lime in the flux has been chemically combined with the aluminates and silicates of the ore and coke ash to form the slag. The compositions of slag that is rich in aluminates and silicates then make it suitable as a raw material for geopolymers. It is a waste and due to its excellent properties, this waste has been synthesised for construction industries and waste water treatment applications. The studies on adsorption ability of slag based geopolymers is still scant. There are some studies shows the ability of geopolymers for heavy metal removal but for GBFS based geopolymers, it is still limited. Hence, the slag based geopolymers is studied for copper removal and purposeful modifying it by using pore forming agent is expected can improve the adsorption capacity.

1.1.2 Introduction to heavy metals

The high concentration of heavy metals in untreated waste water causes a major hazard to the environment. Heavy metals in concerns are Cr, Cu, Cd, Ni, Zn and Pb which have toxic effect to human health and environment. Hence, the concentration of heavy metal has to be reduced to the permissible limits before the effluent is discharged to the rivers.

There are a lot of industries that producing waste water with high heavy metals concentration such as electroplating industries and circuit board printing industries (Barakat, 2011). Copper is the most popular material used in these industries. It is used in providing a highly conductive surface of the electroplating circuits. Besides, it is also used as a bonding wire in the integrated circuits board. For human, copper acted as a trace element in human body and has several functions. It has been used to produce energy in cells, fixing calcium in bones and connective tissue also to help in immune response, nervous system and reproductive system as reported by Morcali et al. (2014). However, if it is congested in excess quantity, it may cause acute poisoning to human body. It also may leads to several mucosal irritation, hepatic and renal damage, liver and brain damages, capillary damages, central nervous problems and gastrointestinal irritation (Tong et al., 2011).

In Malaysia, according to Environmental Quality (Sewages and Industrial Effluents) Regulations 2009, Third Schedule, the permissible concentration of copper in waste water are 0.20 mg/L and 1.0 mg/L for Standard A ad Standard B respectively. Whereas for the purpose of soil irrigation, the permissible limit of copper for plants is 10 mg/L (Ministry of Housing, Netherland, 1994). The e typical quantities of heavy metals in untreated waste water are 1 - 100 mg/L and at neutral or acidic pH values which is less than pH 7.0 (Ayres D. M., 1994). Likewise, sediment samples taken from Juru River, Penang, Malaysia also provided a report showing high copper concentrations in the river. These results were presumed to be due to inappropriate waste management of the nearby industries.

1.1.3 Waste water treatment

There are many methods used for heavy metal removal in waste water but yet, there are disadvantages that accounts for more research on relatively more sustainable and effective ways to treat heavy metals. For instance, chemical precipitation method produces excessive amount of sludge that creates environmental problem on its disposal while ion exchange method is less effective for concentrated metal solution (Al-Harahsheh et al., 2015). Hence, adsorption has become one of the best options for heavy metal removal from waste water due to its simplicity, effectiveness and cost efficiency.

Common adsorbents used in the industry nowadays include activated carbons, zeolites and silica gel. These adsorbents have its own disadvantages even though they are very efficient. As such, the disadvantages of activated carbon is in aspect of cost where it remains as an expensive material even though it gives a large surface area to volume ratio (Khan N. A. et al., 2004; Desta M. B., 2013). Besides, it requires complexing agents for process that involves inorganic matters like metals and it is also not eco-friendly (Tong et al., 2011). Hence, this caused a lot of research interest on low cost adsorbent. Yet still there are some impracticality, for example, the used of chitosan-based adsorbent in waste water treatment is less practical because of its inconsistent source and chitin quality.

Following the discovery of porous structure and adsorption capabilities of geopolymers proven from past studies, GBFS based geopolymers are studied on their adsorption capabilities for copper removal from aqueous solution.

1.1.4 Adsorption using geopolymers

In recent years, geopolymer has studied as a potential adsorbent due to its known amorphous porous structure, corrosion resistant, thermally stable and high tensile strength (Cheng et al., 2012; Mihailova I., 2012). Besides, it consumes low energy consumption and there is no carbon dioxide emission in the preparation

process. Common sources for geopolymers are metakaolin, fly ash and other natural phyllosilicates including slag (Dimitrova & Mehandgiev, 1998; Al-Harahsheh et al., 2015). Table 1.1 summarises the studies on geopolymer as adsorbents for heavy metal removal.

TABLE 1.1 Studies conducted on geopolymeric materials for metals removal

Adsorbent	**Adsorbate**	**Parameter**	**Review**	**Authors**
Metakaolin based geopolymer	Pb2+, Cu2+, Cr3+, Cd2+	Time, Co, pH, Temperature	Pb2+> Cd2+> Cu2+> Cr3+ Pb2+: 100 mg/g	(Cheng et al., 2012)
Metakaolin based geopolymer	Cu2+	pH, adsorbent dosage, contact time, Co	adsorption capacity: 52.63mg/g	(Ge et al., 2015)
Fly ash based geopolymer	Cu2+	Co, pH, temperature, contact time, adsorbent dosage	adsorption capacity at 45 °C: 152 mg/g	(Al-Harahsheh et al., 2015)
Fly ash based geopolymer (Activator: NaOH)	Pb2+	Adsorbent dosage, Co, contact time, pH, temperature	Synthesized geopolymer has higher removal capacity compared with raw coal fly ash Optimum at pH 5	(Kamel et al., 2011)

However, in case of blast furnace slag based geopolymers, the adsorption capabilities for heavy metal removal is still scarcely sufficient. As reported, there is one study by Yu et al. (2015) on the efficiency of granulated blast furnace slag based geopolymer for phosphate removal from industrial waste water.

On the other hand, Li and Zhu (2011) have studied the effect of polyethylene glycol (PEG) in enhancing the porosity of the structure of rice husk char. The results showed that increasing PEG amount could significantly enhance the surface area and other textural properties. Other than that, Cilla et al. (2014) have studied the novel

peroxide route to synthesize a micro/meso-porous geopolymers foam using metakaolin and fly ash based geopolymer. The result shows that a geopolymer foams with total porosity of 85 vol% and high surface area had been successfully synthesized.

1.2 Problem Statement

Current available methods for waste water treatment have their own limitations and disadvantages which include high chemical requirement, formation and disposal of sludge and fouling of membrane (Özçimen & Ersoy-Meriçboyu, 2009). Hence, adsorption using geopolymer is studied because of its high potential to replace current ways of removing heavy metals due to its proven porosity and excellent properties. Several studies show that it indeed has high tensile strength, high resistant to corrosion and thermally stable.

Apart from that, there are few studies on fly ash-based geopolymer and metakaolin-based geopolymer which proved the capabilities of geopolymer in adsorption of heavy metals. One major concern is that to increase the surface area and the porosity of the geopolymers so that the adsorption capacity can be improved. Besides, a study by Li and Zhu (2011) shows that by adding PEG to the rice husk char, it significantly synthesized a porous silica with higher surface area. Moreover, recently there are a few studies reported on foam geopolymer which has increased the surface area and porosity by adding peroxide (Cilla M. S. et al., 2014). Hence, by modifying the geopolymer with these PEG and peroxide (H_2O_2), it is expected to improvise the adsorption capabilities of the geopolymer itself.

Thus, this project will focus on the synthesis of GBFS based geopolymer and its effectiveness in removing copper ions from an aqueous solution. Knowing that different silica ratio synthesis a different forms of geopolymer, this research will vary the silica ratio before choose the highest porosity geopolymers and modify it with pore forming agent; PEG and H_2O_2.

1.3 Objectives

The goals of this study are:

1. To synthesize GBFS-based geopolymer by altering the silica ratio.
2. To modify and determine the effect of adding pore forming agent PEG and H_2O_2.
3. To characterize geopolymers formed in terms of porosity and surface area, surface images, particle size and thermal stability using BET, SEM, PSA and TGA.
4. To study the effect of adsorbent dose, contact time and pH on adsorption of copper from aqueous solution.
5. To study the kinetic model and isotherm of adsorption activities exhibited by GBFS-based geopolymer, PEG incorporated geopolymer and H_2O_2 incorporated geopolymer.

1.4 Scope of Study

This study will focus on the use of GBFS-based geopolymer as adsorbent in copper ions removal. Different samples of GBFS-based geopolymer will be synthesized using different silica ratio. An optimum ratio will be chose before being modified with pore forming agent PEG and H_2O_2.

As described in the objectives, this study will covers the characterization of the geopolymers. Characterization of geopolymers will be done using BET to determine the porosity and surface area of the geopolymer. SEM then will be used to study the surface structure and PSA is to identify the particle size. The thermal stability of the geopolymers then will be studied by using TGA. At last, adsorption studies will be conducted to make a kinetic and isotherm study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Copper ions are toxic substances which presence in the industrial waste water from the industries. Due to their toxic effect to human health and the environment, the concentration of copper in waste water had been controlled tightly. The industry of electroplating and circuit board printing are one of the major sources of copper which contribute greatly to the copper load of industrial waste water (Monser L. & Adhoum N, 2002). In Malaysia, a high level of heavy metals is indicated along the coastal areas of Peninsular Malaysia especially in industrial areas like Bayan Lepas, Kuala Perai, Lumut, Tanjung Harapan and Port Dickson (Zul et al., 2010).

As such, there are standard permissible limit of copper in the industrial waste water prior to their discharge into the fresh water as tabulated in Table 2.1 where it is specified to Standard A and B. According to Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Standard A is applied to inland waters within catchment areas as mentioned in Fourth Schedule in the same regulation while standard B applies to other inland waters.

TABLE 2.1 Acceptable condition for industrial effluent discharge

FIFTH SCHEDULE

[Paragraph 11(1) (a)]

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT FOR MIXED EFFLUENT OF STANDARDS A AND B

Parameter	Unit	Standard A	Standard B
Temperature	˚C	40	40
pH Value	-	6.0-9.0	5.5-9.0
BOD at 20˚C	mg/L	20	40
Suspended Solids		50	100
Mercury		0.005	0.05
Cadmium		0.01	0.02
Chromium, Hexavalent		0.05	0.05
Chromium, Trivalent		0.20	1.0
Arsenic		0.05	0.10
Cyanide		0.05	0.10
Lead		0.10	0.5
Copper		0.20	1.0
Manganese		0.20	1.0
Nickel		0.20	1.0
Tin		0.20	1.0
Zinc		2.0	2.0
Boron		1.0	4.0
Iron (Fe)		1.0	5.0
Silver		0.1	1.0
Aluminium		10	15
Selenium		0.02	0.5
Barium		1.0	2.0
Fluoride		2.0	5.0
Formaldehyde		1.0	2.0
Phenol		0.001	1.0
Free Chlorine		1.0	2.0
Sulphide		0.50	0.50
Oil and Grease		1.0	10
Ammoniacal Nitrogen		10	20
Colour	ADMI*	100	200

ADMI- American Dye Manufactures Institute

Copper removal from industrial waste water can be done using various treatment options that available including chemical precipitation, coagulation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electrodeposition and membrane operations. For conventional treatment plant of copper, most of the industries are using the chemical precipitation methods because it is relatively simple and inexpensive. However, the disadvantageous is that the problem with the precipitate formed that cause disposal problem and the use of hydrogen sulphide (H_2S) in their process.

Nevertheless, with a view to recycle and reuse the wastewater, some treatment plants use adsorption process and adopted it as a single stage treatment instead of the existing chemical methods (Mazumder D. et al., 2011). The most frequently adsorbent used are activated carbon, zeolites and silica gel ((Kazemipour et al., 2008; Hegazi, 2013). Due to some limitations, some treatment plants also use low cost or bioadsorbent which comes from various sources. This necessitated a lot of studies on any potential adsorbents.

Recently, a few studies intensified on the use of geopolymer adsorbent due to its excellent properties and porous structure which similar to zeolites. Besides, Cheng et al. (2012) reported that geopolymers is an excellent properties adsorbent and it is possible to be regenerated which seems promising to be applied in the industry. Lopez F. J. et al. (2014) also reported on geopolymer excellent properties on the matrix compressive strength and its resistance to acid attack, freezing and heat thaw cycles. Such characteristic makes them interesting products for adsorbents and the regenerated matrix could become the main advantages of it. Moreover, the use of pore forming agent in the geopolymer could enhance the surface area and porosity as reported by Li and Zhu (2011) and Cilla et al. (2014) which could be advantageous for heavy metal copper removal via adsorption.

2.2 Heavy Metal Contaminated Waste Water

The quantity of heavy metals contaminated wastewater that been discharged into the environment gets increasing. These happen especially in developing countries due to the rapid industrialization (Bilal et al., 2013; Vafakhah et al., 2014). The industries that has high contributions to these problems are metal plating industries, circuit board printing industries, mining operations, fertilizer industries, batteries industries, paper industries and pesticides (Fu & Wang, 2011; Cheng, 2012). The presence of the heavy metals generated by these industries causes hazard to the water environment due to their toxic effect to human health and other organisms (Morcali et al., 2014; Jiang et al., 2015).

It is becoming worst when some irresponsible party improperly dispose the untreated wastewater into the rivers which can cause soil contamination in case of soil irrigation and results in severe environmental damage (Oğuz et al., 2003; Ali et al., 2012). These may cause the heavy metals to accumulate in plants' part, and finally pose serious health hazard to human beings and the animals once it is consumed (Hashim et al., 2011). Also, because of their high solubility in the aquatic environments, heavy metals also cause hazards to the aquatic living organisms. Heavy metals in concern for treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium (Wan Ngah & Hanafiah, 2008; Barakat, 2011).

Copper is one of the most toxic heavy metal to living organisms. By not treating well the industrial waste water prior to the discharge to the river, it will affected the aquatic organism and human as well through the food chain. By being exposed to copper, human will experience health problem such as stomach ache, irritation of nose, mouth, eyes and headache (Vafakhah et al., 2014). Bilal et al. (2013) added that high exposure of copper to human also will cause severe mucosal irritation, capillary damage, hepatic and renal damage and central nervous system irritation.

2.3 Waste Water Treatement

There are a lot of waste water treatment options available such as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation and membrane operations. However, most of the industries are using the chemical precipitation methods because of it is relatively simple and inexpensive. The chemical precipitation methods occur through the use of several unit operations, as displayed in Figure 2.1 (Wang et al., 2004). There are points in the treatment process where the pH is adjusted to ensure adequate metals and metals solids removal. The pH is adjusted by controlling the hydroxide ion concentration of the water so that the metals will form insoluble hydroxide precipitates. Once the metals form precipitate, then it is removed, and the water, now with low metal concentrations, can be discharged.

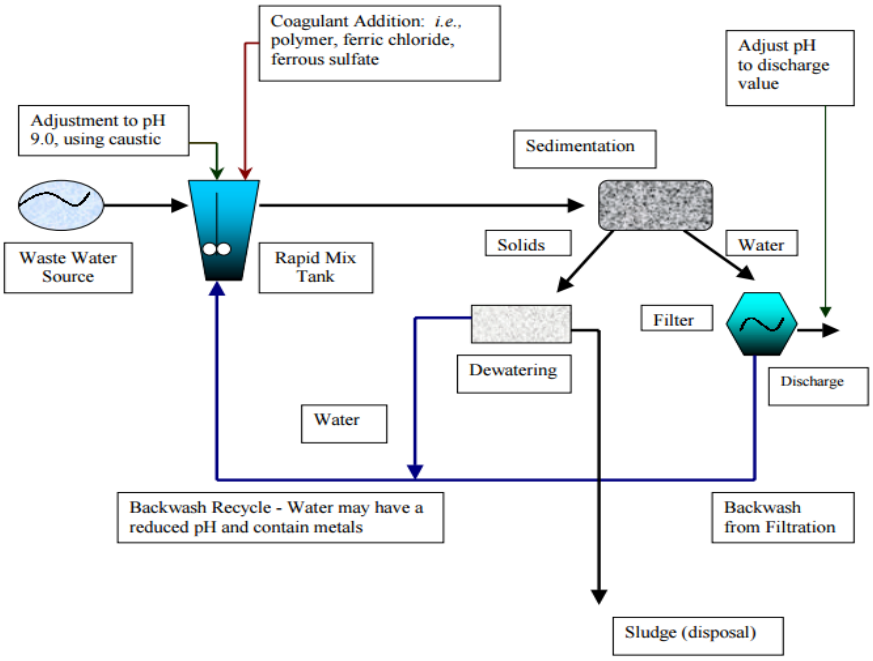

FIGURE 2.1 Conventional chemical precipitation treatment plant

Metal precipitation is primarily dependent upon two factors: the concentration of the metal and the pH of the water. The typical quantities of heavy metals in untreated waste water are 1 - 100 mg/L and at neutral or acidic pH values which is less than pH 7.0 (Ayres D. M., 1994). However, for copper concentration from electroplating industries is typically 37 mg/L (Monser L. & Adhoum N., 2002).

Hence for chemical precipitation methods, when caustic is added to water which contains dissolved metals, the metals will react with the hydroxide ions to form metal hydroxide precipitate that is high in pH.

According to Wang et al. (2004) and Fu and Wang (2011), this technique is effective and by far is the most widely used process in industry to remove metals because it is relatively simple and inexpensive. However, its disadvantages is that metal precipitates may be formed and cause disposal problems in either the settling and filtration process. Besides, previous study by Jiang et al. (2015) showed that for copper removal using hydroxide precipitation use hydrogen sulphide as the precipitants that results in the evolution of toxic H_2S fumes.

Moreover, there are also other methods that are available in the industries such as ion exchange and membrane filtration and others. Yet still every methods has its own advantages and disadvantages (Barakat, 2011; Cheng et al., 2012; Shrestha et al., 2013). Table 2.2 shows the comparison of these various techniques available for metals removal as studied by Bilal et al. (2013).

TABLE 2.2 Copper ion removal technique

Processes	Advantages	Disadvantages
Chemical precipitation	• Adapted for large quantities • Simple to use	• High chemical requirement • Sludge disposal problem • Temperature, pH and concentration difficult to be monitored
Ion exchange	• High treatment capability • Higher rate of metal removal	• Not for large scale • Costly synthetic resins
Membrane filtration	• Reuse of wastewater • Recovery of valuable material	• Membrane fouling • High capital cost, maintenance and operational cost • Less efficient in low concentration
Coagulation/ flocculation	• Applicable to large scale wastewater treatment	• Costly reagents • Large sludge production • Disposal issues
Electrolytic recovery	• Less chemical consumption • Recovery of pure metal • Effective removal of desired metal	• Energy costs • High capital cost • Reduced efficiency at dilute concentration • Cannot be applied to higher quantity of wastewaters
Reverse osmosis	• Effective removal of metals	• High costs of chemicals • Fouling of membranes
Adsorption	• Highly effective	• Disposal of exhausted adsorbents

Nevertheless, with a view to recycle and reuse the wastewater, some treatment plants use adsorption process and adopted it as a single stage treatment instead of the existing chemical methods (Mazumder D. et al., 2011). A lot of reviews show that adsorption is the most attractive as compared to other options due

to the cost effective, sustainable, protocol simplicity and the availability of eco-friendly bioadsorbents (Özçimen and Ersoy-Meriçboyu,. 2009; Fu & Wang, 2011; Cheng, 2012; Bilal et al., 2013). It offers flexibility in design and operation while gives high quality treated effluent. In order to overcome the disadvantages on disposal of exhausted adsorbents, the adsorbent may be regenerated using suitable desorption process as reported by Wan Ngah and Hanafiah (2008).

2.4 Adsorption

2.4.1 Adsorption theory

Adsorption is a separation process that occur when a gas or liquid solute called adsorbate accumulates on the surface of a solid or a liquid adsorbent (Geankoplis, 2003). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Meanwhile, adsorption only occurs at the surface of a particle. When the adsorbent become saturated with the solute (components to be removed), the adsorbent can be regenerated by acid-wash or water-wash. The mechanism of adsorption process consists of three steps which are diffusion, migration and adsorption process as displayed in Figure 2.2.

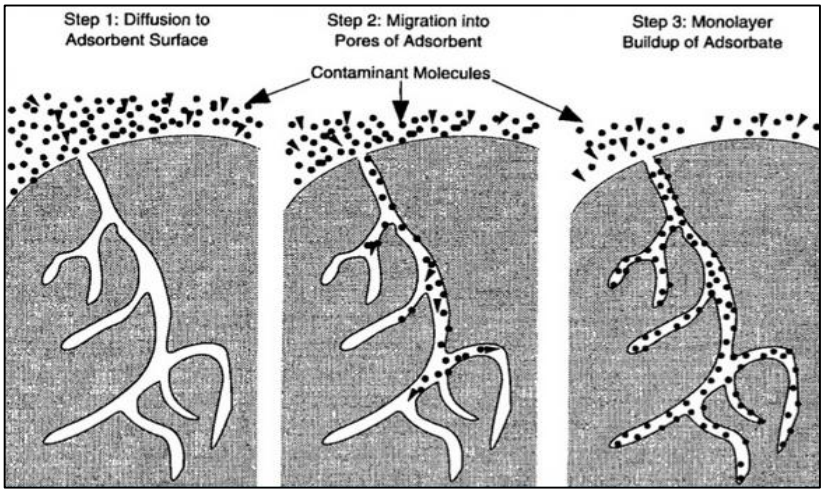

FIGURE 2.2 Adsorption mechanism

2.4.2 Types of Adsorptions

There are two types of adsorption which are physisorption and chemisorption. In physisorption, there is only a Van der Waals force of attraction between the adsorbent and the adsorbate where both the reacting molecular species are chemically unaltered. For chemisorption, there are new chemical bonds created between the adsorbent and the adsorbate which means chemical reaction is occurred, as opposed to the Van der Waals force.

The types of adsorption is depending upon the types of adsorbate involved and their respective reaction with adsorbent. Table 2.3 shows the differences between physisorption and chemisorption.

TABLE 2.3 Difference of chemisorption and physisorption (Geankoplis, 2003)

Physisorption	**Chemisorption**
Low enthalpy of adsorption (5–50 kJ/mol)	High enthalpy of adsorption (200–400 kJ/mol)
Reversible process	Irreversible process
Intermolecular forces of attraction are van der Waals forces	Valence forces of attraction are chemical bond forces
Multi-molecular layers formed	Monomolecular layer formed
Preferable of low temperature	Preferable of high temperature
Not specific process	Highly specific process

2.4.3 Types of Adsorbents

Adsorbents are materials which have porosity in their structure and have pore volumes of up to 50% of total particle volume (Geankoplis, 2003). Adsorbents supposed to have the ability to extract gases, liquids or solids. It also will not change in physical properties during the adsorption process.

Adsorbents are classified according to their pore sizes, nature of surfaces and nature of structures. The classification of pore size as recommended by International Unit of Pure and Applied Chemistry (IUPAC) is often used to delineate the range of pore size (d is the pore diameter).

Micropores $d < 2nm$
Mesopores $2 < d < 50$ nm
Macropores $d > 50$ nm

Adsorbent is normally in the form of small particles, pellets, beads or granules that sized from 0.1 mm to 12 mm. It is often used as packing beds in an adsorption column.

Various adsorbents are used in the industry such as activated carbons, zeolites and silica. Nevertheless, researchers continually study on better adsorbent using various raw materials such as agricultural waste, industrial by-products, natural materials and modified biopolymers in order of searching a lower cost yet effective adsorbents (Barakat, 2010). An adsorbent is termed as a low cost adsorbent when it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Ahmad K. et al., 2004). Some of the potential adsorbent that have been studied for copper removal is tabulated in Table 2.4.

TABLE 2.4 Studies on potential of natural substances for copper removal

Adsorbent	**Adsorbate**	**Parameter**	**Review**	**Authors**
Poly aniline graft chitosan beads	Cu2+ ions	Adsorbate dosage, pH	flakes are converted into chitosan gel beads adsorption capacity: 13 mg/g	(Igberase et al., 2014)
Precursor hazelnut husks	Cu2+ and Pb2+ ions	pH, contact time, adsorbent dosage and initial metal concentrations	adsorption capacity: 6.645 and 13.05 mg/g	(Imamoglu & Tekir, 2008)
Tea waste	Cu2+ and Pb2+ ions	pH, adsorbent dosage, initial metal concentrations	adsorption capacity: 48 and 65 mg/g for Cu and Pb	(Amarasinghe and Williams R. A., 2007)
Sawdust	Cu2+ ions	sulphuric acid treated sawdust (SDC) and untreated (SD)	Sulphuric acid treated sawdust is much better. maximum adsorption: SDC: 95.7% SD: 71.7%	(Senin H. B. et al., 2006)
Wheat bran	Cr(III), Hg(II), Pb(II), Cd(II), Cu(II), Ni(II)	pH of solution, effect of various treatments	adsorption capacity: 93 mg/g Cr(III), 70 mg/g Hg(II), 62 mg/g Pb(II), 21 mg/g Cd(II), 15 mg/g Cu(II)	(Farajzadeh M. A. and Monji A. B., 2004)

			and 12 mg/g Ni(II)	
Rice husk	Cu2+	pH: 5.2-5.3 Modifying agents: Tartaric acid (TA)	adsorption capacity: 29 mg/g	(Wong et al., 2003)

2.4.4 Equilibrium Isotherm for Adsorption

The equilibrium relationship between the adsorbent concentration and adsorbate concentration in adsorption process can be related using three isotherms which are linear isotherm, Freundlich isotherm and Langmuir isotherm as figured in Figure 2.3.

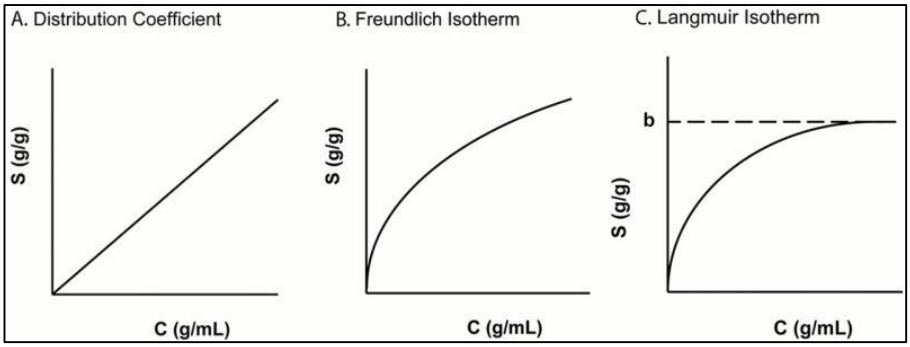

FIGURE 2.3 Adsorption isotherm types

2.4.4.1 Linear Isotherm

From Figure 2.3, the linear isotherm defines relationship between q (g adsorbate/g adsorbent) and c (g adsorbate/mL fluid). The relationship can be expressed using Equation 1.

$$q = Kc \quad (1)$$

K is a constant expressed in mL/g adsorbent. This linear isotherm is not common in the entire adsorption process, but it is applied for dilute region in adsorption process to determine data for many systems.

2.4.4.2 Freundlich Isotherm

The Freundlich isotherm is mostly applicable to physical adsorption and useful for liquid system. Equation 2 shows the relationship of q and c for Freundlich isotherm.

$$q = Kc^{n} \tag{2}$$

The value of K and n is determined graphically, providing a series of q and c value determined through experiment.

$$\log q = \log K + n \log c \tag{3}$$

By plotting graph of log q against log c, the slope of the graph will be the value of n while the y-intercept of the graph will be the value of logarithm K according Equation 3.

2.4.4.3 Langmuir Isotherm

The Langmuir isotherm is the strongly favourable type of isotherm for an adsorption process. Equation 4 shows the relationship between q and c in Langmuir isotherm.

$$q = \frac{q_o + c}{K + c} \tag{4}$$

q_o is expressed as kg of adsorbate/kg solid while K is g/mL. The equation is applied with assumption of monolayer adsorption, actives sites on adsorbent are fixed, adsorption reached equilibrium and adsorption process is reversible. The value of qo and K can be determined by plotting graph of 1/q versus 1/c according to Equation 5.

$$\frac{1}{q} = \frac{K + c}{q_o c} = \frac{k}{q_o}\left(\frac{1}{c}\right) + \frac{1}{q_o} \tag{5}$$

The slope is K/q_o and intercept is $1/q_o$ (Geankoplis, 2003).

2.4.5 Kinetic Studies for Adsorption

It is important to identify the adsorption mechanism type by the kinetic studies in a given system. This is because from it, the rate-controlling steps that include mass transport and chemical reaction process can be known to test the experimental data. In kinetic modelling, the pseudo-first and -second order equations are the most celebrated models for explaining the biosorption of heavy metal (Febrianto J.et al., 2008).

2.4.5.1 The Pseudo-first-order kinetic studies

Hypothetically, to ascertain the rate constants and equilibrium metal uptake, the straight-line plots of log (q_e −q) against t of Equation 6 were made at different initial metal concentrations.

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{6}$$

The q_e value acquired by this method is then contrasted with the experimental value. If large discrepancies are posed, the reaction cannot be classified as first-order although this plot has high correlation coefficient from the fitting process.
Some studies will shows that q_e values lower than the experimental values. This is probably caused by a time lag, which is due to the presence of boundary layer or external resistance controlling at the beginning of the sorption process.

2.4.5.2 The Pseudo-second-order kinetic studies

For pseudo-second-order kinetic studies, the equation in linear form is as shown in Equation 7.

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 \, {q_e}^2} \tag{7}$$

The pseudo-second-order rate constants were determined experimentally by plotting t/q against t. This tendency comes as an indication that the rate limiting step in biosorption of heavy metals are chemisorption involving valence forces through the sharing or exchange of electrons between sorbent and sorbate (Febrianto J.et al., 2008).

2.4.6 Factors Affecting Adsorption

There are few factors which affect the adsorption process other than the qualities of adsorbent itself which are dosage of adsorbents, pH, temperature, salinity, contact time, initial concentration of adsorbates and ionic strength (Wang & Peng, 2010; Al-Harahsheh et al., 2015).

The most important parameter that should be considered prior to adsorption are adsorbent dosage. Studies by Imamoglu M. & Tekir O. (2008), Cheng T. W. (2012) and Javier L. (2014) show that the rate of adsorption would increase significantly with the increase of adsorbent dosage as more adsorbents provide more binding sites for adsorbates. However, the consumption of adsorbents have to be considered to achieve economical balance between removal efficiency and cost optimization.

Furthermore, past studies reported the adsorption of copper is found to be increase with the increase in contact time but become constant after a period of time where equilibrium is achieved. The more the contact time, the more adsorbates will be adsorbed on the adsorbents until equilibrium is achieved where the adsorbents are fully saturated with adsorbates on its surface.

Other than that, the influence of pH also is important prior to adsorption where it would affect both aqueous chemistry and surface binding sites of the adsorbent (Igberase, Osifo, & Ofomaja, 2014; Ge et al., 2015; Al-Harahsheh et al., 2015). Moreover, a change in pH also results in change in the charge profile of adsorbate species, which consequently influences the interaction of adsorbate and adsorbent. According to Dimitrova and Mehandgiev (1998), studies have shown that

sorption of heavy metals is most effective in an alkaline medium; while at pH below 5.0 sorption is negligible due to the competitive effect of hydrogen ions. Al-Harahsheh et al. (2015) also reported the same trend of copper adsorption on fly ash.

2.4.7 Geopolymer as adsorbent

Geopolymer has been used up for many applications such as construction industry, heavy metal immobilisation application and archeology. It has found that the geopolymer has porosity structure that are formed during the geopolymerization process which make it applicable for heavy metal removal application. The excellent properties and high performance in terms of short curing time and high tensile strength of the geopolymers is the added advantage of it as an adsorbents. Moreover, it has high thermal stability and high resistant to corrosion which also make them a superior option.

Nevertheless, in recent years, GBFS based geopolymers were synthesized for utilization in heavy metals immobilization using adsorption process. As such, a study reported that it exhibits high adsorption capacity in lead ions removal from an aqueous solution (Mihailova I. et al., 2013). It has been established from the studies that by increasing the surface area, the adsorption capacity of lead is increasing.

On the other hand, Li and Zhu (2011) have studied the effect of polyethylene glycol (PEG) in enhancing the surface area of rice husk char. It is reported that increasing the PEG will enhance the surface area and the other textural properties. However, the studies of adding it to the modified geopolymer is still scant. Furthermore, Cilla M. S. et al. (2014) has studied the use of combined route of saponification, peroxide and gelcasting to produce geopolymer foams with total porosity of 85 vol%. Both of these study could be modified to the GBFS geopolymer and it could enhance the removal of copper from aqueous solution.

2.5 Geopolymer

2.5.1 Background of Geopolymer

History of geopolymers can be traced back to late 1970s, developed by J. Davidovits. Geopolymers are kinds of inorganic polymers that have been gradually attracting world attention as potentially revolutionary materials. It is a class of three-dimensionally networked alumino-silicate materials which have similar structure as natural zeolite minerals (Cheng T. W., 2003). It is also identified as a family of amorphous alkali or alkali-silicate activated aluminosilicate binders. The material is made up of a polymeric Si-O-Al functional group that creates a framework likely to zeolites, but more amorphous instead of crystalline.

Geopolymers can be synthesized easily under normal ambient temperature using different raw materials, for instance fly ash and metakaolin. Both raw materials have high aluminosilicate content and highly favourable for the synthesis of geopolymers. Any other aluminosilicate materials which are rich in Si and Al also can be synthesized to geopolymers.

2.5.2 Geopolymerization

Geopolymerization is a geo-synthesis reaction involving silica-aluminate sources that will be dissolving in an acid or alkaline solution to form SiO4 and AlO4 tetrahedral units. This is supported by Javier L. (2014) which stated that the term *geopolymer* represent an inorganic polymer constituted by SiO_4 and AlO_4 tetrahedral and were formed by the reaction of polycondensation with an alkaline solution such as sodium hydroxide or sodium silicate that is called activator. The silica ($SiO_{2)}$ and alumina (Al_2O_3) species present in the raw materials react in a highly alkaline medium, organizing themselves in a continuous three dimensional structure by sharing oxygen atoms, forming bonds such as Si–O–Al–O, Si–O–Al–O–Si–O or Si–O–Al–O–Si–O–Si–O (Davidovits, 2011).

The mechanism of geopolymerization is summarized in figure 2.4 (Gupta, 2012). The geopolymerization process is divided into three stages which are destruction-coagulation, coagulation-condensation and condensation-crystallization. The destruction-coagulation stage is where the dissolution of the solid aluminosilicate source occurs by alkaline hydrolysis that will produce numerous aluminate and silicate species. A supersaturated aluminosilicate solution that formed will result the formation of gel. In the gel formation phase, the oligomers of aluminate and silicate species continue to rearrange and reorganized as the connectivity of the gel network increase. Finally, a three-dimensional aluminosilicate network is formed and attributed as geopolymer.

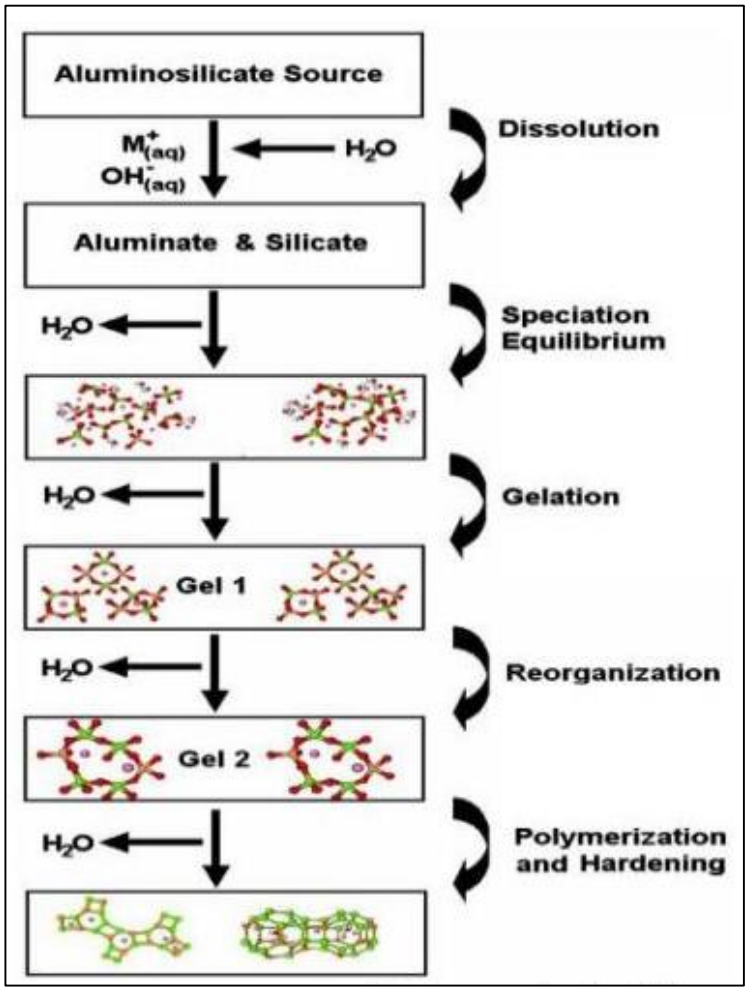

FIGURE 2.4 Geopolymerization mechanism

2.5.3 Raw Material and Activator

The most commonly used raw material for geopolymerization would be metakaolin and fly ash. Besides that, any other materials which are rich in aluminium and silica also can be used as raw material for geopolymerization such as blast furnace slag. The blast furnace slag mainly composed of the oxides of calcium, silicon, iron and manganese that make it suitable to be synthesized as geopolymer. It also contain much reactive SiO_2 and Al_2O_3 which can be a good raw material (Yunsheng et al., 2007).

Currently most of the slag is utilized in fields of Portland cement industry or concrete production company. Jha et al. (2008) also supported that the blast furnace slag has been utilized in cement manufacturing, road building applications and civil construction industry. Those properties of slag which are high strength, hardness and wear resistance and good durability properties have allowed slag to be used successfully in those applications (Fredericci et al., 2000; Zhao et al., 2015).

Activator is another important element in geopolymerization. Activators presence in the process to balance the negative charge of aluminium (Al-Harahsheh et al., 2015). A commonly used activator in geopolymerization is alkaline solution such as sodium hydroxide or potassium hydroxide solution (Rattanasak & Chindaprasirt, 2009; Zhang et al., 2009; Somna et al., 2011).

2.5.4 Synthesis of GBFS Based Geopolymer

Blast furnace slag is a by-product in the production of pig iron which causes a disposal problem. GBFS is rich in SiO_2 and Al_2O_3 which make it a good raw material to be synthesized to geopolymer. The process synthesis of GBFS based geopolymer can be done by adding GBFS to alkaline activator at ambient temperature before being cured in an oven for some time.

The alkaline activator usually be used are sodium hydroxide (NaOH) or potassium hydroxide (KOH). The sodium cations presence in the activator do not

take part in polymerisation reactions, but function only as an activator, destroying the slag structure to release Ca, Si and Al species. Then, the Al species will substitutes the Si at the “bridging” tetrahedral forming a polymeric linkages –Si-O-Si-O-. The reaction product is a form of calcium silicate (substituted by aluminium) which is similar to the calcium silicate hydrate (CSH) formed in cement materials (Oh et al., 2010).

Due to the various composition in the raw material for geopolymerization, some studies added sodium silicate (Na_2SiO_3) to the alkaline activator to increase the silica components in the geopolymers. Some studies proved that silica amounts effect the strength of the geopolymers. By increasing the silica amounts in the alkaline activator, the development of strength increase (Chindaprasirt P. et al., 2012). The study also reported that the silica effect the setting time for raw materials that is high calcium-based system unlike conventional geopolymers system. The setting time will be decreased due to the formation of CSH and CASH which could be an advantageous for GBFS based geopolymers that is high in calcium content.

In term of effectiveness for the copper removal, as mentioned in earlier section, PEG and H_2O_2 are used to create a porous silica with high surface area and foam geopolymer with high porosity, respectively. So, it is expected by modify the GBFS based geopolymer with these, the surface area, porosity and the effectiveness of copper removal can be improved.

CHAPTER 3

METHODOLOGY

3.1 Overview

The research work of this study is divided into four main stages, which are to synthesis and select the optimum silica ratio, to study the effect of adding pore forming agent (PEG and H_2O_2) into the optimum ratio, to characterize the geopolymers and experimental testing of copper sulphate solutions on geopolymers as displayed in Figure 3.1.

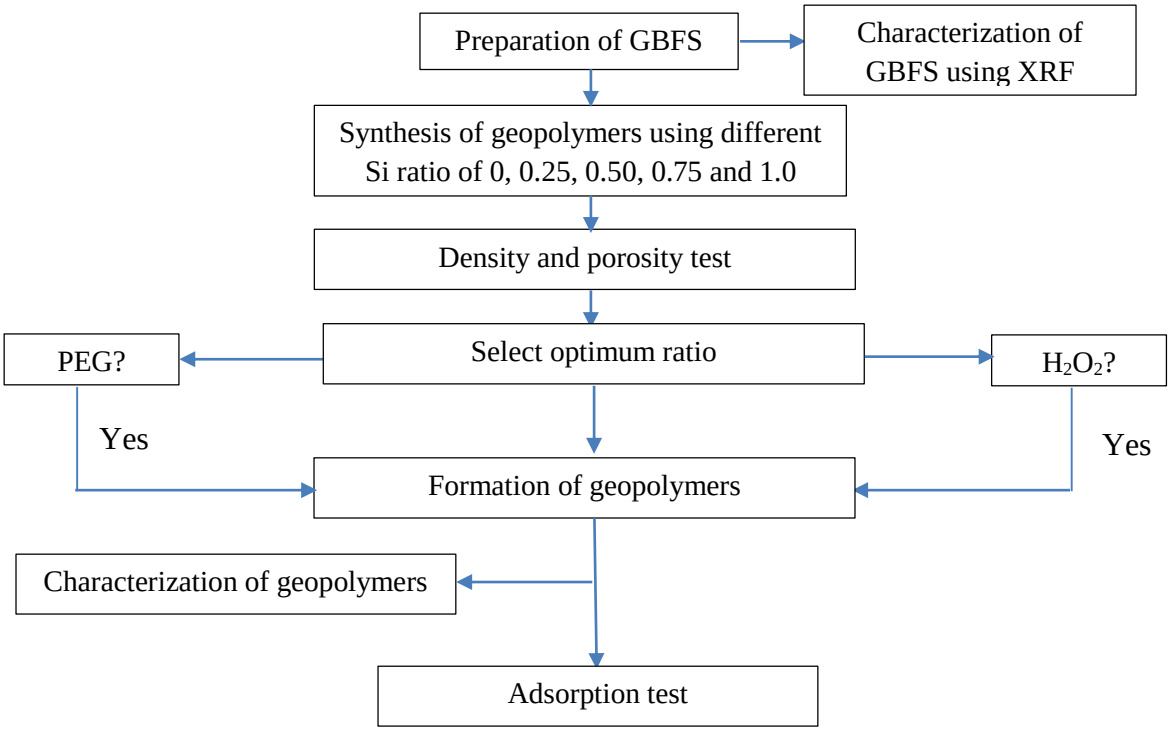

FIGURE 3.1 Summary of research methodology

3.1.1 Materials

Granulated Blast Furnace Slag (GBFS) which is the raw materials for geopolymerization was available in UTP laboratory. Distilled water and analytical grade sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) were used in all experiments. Moreover, copper sulphate ($Cu_2SO_4.5H_2O$) solution will be used in the batch adsorption test. The solution will replicate the industrial waste water from electroplating industry in Malaysia.

3.2 Preparation and Characterization of Raw Material

The raw material GBFS is mixed thoroughly before being collected for sampling. The composition of GBFS then is characterized using XRF. The characterization is essential to identify the amount of sodium silicate (Na_2SiO_3) to be added to form desired geopolymer.

3.3 Synthesis of GBFS-based Geopolymer

In this step, the activator used is sodium hydroxide (NaOH). Sodium silicate (Na_2SiO_3) amount will be varied due to different NaOH:Na_2SiO_3 ratio as shown in Table 3.1. The geopolymer then will be characterized based on different Si ratio.

1. NaOH was first dissolved in 1000 ml water solution at 20°C to get 8M of NaOH.
2. The NaOH solution and Na_2SiO_3 were mechanically mixed based on the ratio and stirred for about 3 minutes to create a homogenous alkaline activator solution.
3. The homogeneous paste of mixed alkaline activator and GBFS were immediately casted into plastic cylindrical moulds.
4. The mixture then will be placed in a 40°C oven to solidify.
5. The curing time usually take about 3 days.
6. Geopolymer formed was then crushed and sieve to get uniform size (<200µm).

TABLE 3.1 Mixed design of different Si ratio

Geopolymer	**Water:GBFS ratio**	**NaOH:Na_2SiO_3 ratio**
GP-1.0	1:1.8	1:1
GP-0.75	1:1.8	1:0.75
GP-0.5	1:1.8	1:0.50
GP-0.25	1:1.8	1:0.25
GP-0.0	1:1.8	1:0

3.4 Selection of Optimum Si Ratio

The synthesized geopolymers were analysed based on its density and porosity calculation to select the optimum ratio of GBFS based geopolymer. The porosity can be calculated using Equation 8 below.

$$Porosity = \frac{Powder\ density - Bulk\ density}{Powder\ density} \quad (8)$$

3.5 Adding Pore Forming Agent to the Modified Geopolymer

The pore forming agent used are poly-ethylene glycol (PEG) and hydrogen peroxide (H_2O_2). The amount of PEG used are 3% based on a study by Li and Zhu (2011). Besides, 8% of H_2O_2 were added referring to a study by Cilla et al. (2014). The pore forming agent is mixed after the slurry mixture is formed between GBFS and alkaline activator.

3.6 Characterization of Geopolymer

3.6.1 Determination of composition

X-ray Fluorescence analysis (XRF) works in a way where X-ray is being emitted from source to the sample, ionizing the components atom. XRF detects type of radiation which is specific and special to each type of material and characterize the identity of element within sample. XRF is used in this project to determine the composition of the GBFS before it is synthesized to geopolymer.

3.6.2 Determination of porosity and surface area

The surface porosity and specific surface area of respective geopolymers was determined through Brunauer, Emmett and Teller (BET) analysis. The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface.
The process of characterization is listed below:

1. The geopolymer formed was crushed to size of less than 200 μm.
2. The density and weight of samples were determined.
3. The sample was then being placed in the sample holder of BET for analysis.

3.6.3 Determination of surface image

The surface image of geopolymers was generated by Scanning Electron Microscopy (SEM). Sample powders were first coated with a layer of conductive material in a sputter coater before being placed under the SEM for analysis.

3.6.4 Determination the size of a particulate solid

Particle Size Analysis (PSA) is used to determine the size of a particulate solid. It will give the results of volume of particulates with respect to their size range. The sample dispersion unit is segregated and attached to the optical bench. The laser

beam will lights up the samples and a detector will measure the intensity of scattered light.

3.6.5 Determination of thermal stability

Simultaneous thermogravimetric analysis (TGA) were performed to study the thermal stability up to 800ºC. In this TGA test, the mass loss was measured while the specimens were gradually exposed to increasing temperatures. Powdered specimens were used in TGA to ensure the achievement of thermal equilibrium during transient heating.

3.7 Batch Adsorption Test

The adsorption experiments were conducted using synthesized geopolymers as adsorbent while copper ion in $Cu_2SO_4.5H_2O$ solution as adsorbate. The adsorption experiment design is summarized in Table 3.2.

TABLE 3.2 Experiment design of adsorption experiment

Investigated parameter	Initial copper concentration (ppm)	Temperature (ºC)	pH	Contact time	Adsorbent dosage (g)
Adsorbent dosage	50	25	Natural	240	0.2, 0.4, 0.6, 0.8, 1.0
Contact time	50	25	Natural	120, 150, 180, 210, 240	Best dosage
pH	50	25	3, 5, 7, 9, 10	Best time	Best dosage

3.7.1 Effect of adsorbent dosage

Different adsorbent dosage at same pH value and contact time, a higher adsorbent dosage will adsorb more adsorbates and achieve equilibrium at a shorter time.

1. 100 ml of 50 ppm of $Cu_2SO_4.5H_2O$ solution was measured and put in a conical flask.
2. 0.2 g of GP-25:75 was weighed and added in the conical flask.
3. The conical flask was then put in shaker for 240 minutes with setting of 25°C and 150 rpm.
4. The solutions from the conical flask were obtained and being centrifuged to separate the copper solution from adsorbent.
5. Copper solutions obtained were analysed using MP-AES to determine the concentration.
6. The experiment is repeated with different adsorbent dosages.

3.7.2 Effect of contact time

Different adsorbent adsorb at different rate, a more effective adsorbent is able to adsorb more adsorbates and achieve equilibrium at a shorter contact time.

1. 100 ml of 50 ppm $Cu_2SO_4.5H_2O$ solution was added into a conical flask.
2. 0.1 g of adsorbent dosage was then measured and added into the conical flasks containing copper solution.
3. The conical flask was then put in shaker with setting of 25°C and 150 rpm.
4. The timer was started.
5. A contact time of 240 minutes is allowed for adsorption to occur.
6. 5 ml of solution was extracted at each 120, 150, 180, 210 and 240 minutes.
7. Solutions obtained were analysed using MP-AES to determine the concentration.
8. The experiment is repeated with different pH value.

3.7.3 Effect of pH

As the pH of solution has a significant effect on the adsorption activities of the adsorbents, the effect of pH on copper removal percentage is studied here in this research as well.

1. 100 ml of 50 ppm $Cu_2SO_4.5H_2O$ solution was added into 5 conical flasks.

2. The pH of solutions were measured and adjusted to 3, 5, 7, 9 and 10 by adding 0.1 M hydrochloric acid (HCl) or 0.1M sodium hydroxide (NaOH).
3. The best of adsorbent dosage from previous test was then measured and added into the conical flasks
4. The conical flask was then put in shaker with setting of 25°C and 150 rpm.
5. The timer was started.
6. A contact time of 240 minutes is allowed for adsorption to occur.
7. Resulting solutions from conical flasks were obtained and being centrifuged to separate the copper solution from adsorbent.
8. Solutions obtained were analysed using MP-AES to determine the concentration.

3.7.4 Determination of copper concentration

The concentration of the $CuSO_4$ solution will be analysed before and after the adsorption test. The solutions are analysed using mass plasma-atomic emission spectroscopy (MP-AES) analysis.

3.7.5 Equilibrium Isotherm and Kinetic Study

Experimental data obtained from the experiments will be used to determine which isotherm model that the adsorption activities of the geopolymer samples are fitted to. The calculation process was aided with Microsoft Office Excel Spreadsheet.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Raw Material

Before the GBFS geopolymer is synthesized, the sample is characterize using XRF analysis. Table 4.1 shows the result of the XRF analysis.

TABLE 4.1 Chemical compositions (%) of GBFS

COMPONENTS	**COMPOSITION (%)**
CaO	69.4
SiO_2	17.9
Al_2O_3	4.01
MgO	2.37
Fe_2O_3	2.18
SO_3	1.97
P_2O_5	0.921
MnO	0.472
TiO_2	0.456
ZnO	0.138
SrO	0.0369
Cr_2O_3	0.0247
K_2O	0.0223
CuO	0.0119

Result from the XRF analysis shows that the GBFS is mainly made of CaO followed by SiO_2. This is close to previous research findings by Gardner et al. (2015) where the GBFS shows composition of 40.2% CaO, 36.6% SiO_2, 12.0% Al_2O_3 and 7.9% MgO.

4.2 Preparation of Geopolymers

4.2.1 Synthesised of raw GBFS-based geopolymer

. Figure 4.1 shows the different forms of geopolymers formed with decreasing silica ratio of alkaline activator.

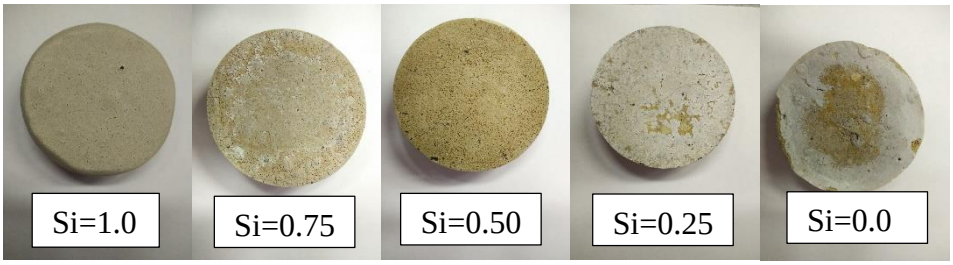

FIGURE 4.1 The synthesized geopolymers with different Si ratio

As observed from Figure 4.1, the surface roughness increases with decreasing silica ratio in the alkaline activator. This is due to the less silica, the less formation of bonding in the geopolymer system and the longer the setting time (Hawa A. et al., 2013). Hence, to pick the best ratio, density test and porosity test is conducted.

4.2.1.1 Density and porosity test

Bulk density is tested using the mass and volume occupied in the container. The powder density is done by using Ultrapycnometer 1000 Version 2.2. The equipment is used to determine the nitrogen and helium-based coal densities. The gas which displaces fluid can penetrate very fine pores. The density and porosity calculated value for all the mixed design geopolymers are summarised in Table 4.2.

TABLE 4.2 Bulk density of geopolymer

Sample	**Avg. Weight (g)**	**Bulk Density (g/cm^3)**	**Powder Density (g/cm^3)**	**Porosity (%)**
Si=0.1	64.90	1.75	2.62	33.00
Si=0.75	63.19	1.76	2.82	40.42
Si=0.5	63.04	1.62	2.71	40.41
Si=0.25	67.00	1.72	2.52	31.71
Si=0.0	73.56	1.67	2.63	36.49

The result tabulated shows that sample GP-0.75 with Si ratio of 0.75 has the highest porosity. Hence, to improve the porosity and to create a novel foam geopolymer, the procedure is further improved by adding poly ethylene glycol (PEG) and hydrogen peroxide (H_2O_2) in a separate samples.

4.2.2 Synthesised of PEG incorporated geopolymer

The amount of PEG added to the modified geopolymers is about 3% based on research works done by Li and Zhu (2012).

4.2.3 Synthesised of H_2O_2 incorporated geopolymer

By referring to a study by Cilla et al. (2014), different height of geopolymers foams is synthesized using different percentage of H_2O_2 amount added. The result is summarised in Table 4.3 and Figure 4.2 shows that maximum height is formed when it is modified with 8% of H_2O_2. After 8%, the result shows that the height stop increasing and reduced. This is due to a very big bubble of air formed and get exploded thus retard the height of geopolymer.

TABLE 4.3 Different percentage of adding H_2O_2

Sample	Percentage of H_2O_2 (%)	Geopolymer height (cm)
GP-H_2O_2 4%	4	1.9
GP-H_2O_2 6%	6	3.9
GP-H_2O_2 8%	8	4.8
GP-H_2O_2 10%	10	3.8
GP-H_2O_2 12%	12	4.2

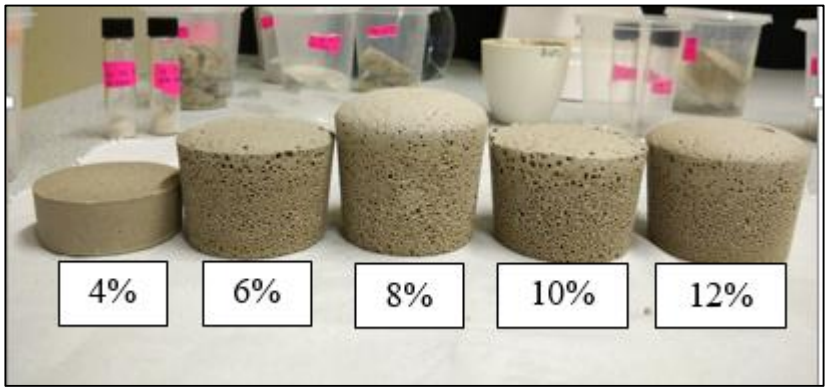

FIGURE 4.2 Different height of geopolymer foams were synthesized

4.3 Characterization of Geopolymers

The porosity, surface area, surface images, particle size and the thermal stability of the geopolymers synthesised had been studied using different analytical tools and techniques. An important property for an effective adsorbent are the surface area and pore volume. However, the particle size is also an important factor in adsorption. The thermal stability then will prove that the geopolymer adsorbents is suitable to be used at high temperature.

4.3.1 BET analysis

In order to predict the adsorption capabilities of the geopolymer synthesized, BET is used to measure the physical adsorption test gas molecules on its surface and to measure the specific surface area. BET works by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The amount of gas adsorbed at a given pressure allows to determine surface area. This occurs on the outer surface and, in case of porous materials, also on the surface of pores. It occurs at a temperature of 77 K and leads to a so-called adsorption isotherm, sometimes referred to as BET isotherm. The results from the BET analysis are shown in Table 4.4.

TABLE 4.4 BET surface area, pore volume and pore size

Sample	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (Å)**
GP-0.75	1.9354	0.007123	140.8258
GP-0.75 PEG	5.5525	0.017018	122.6004
GP-0.75 H_2O_2	2.0646	0.006235	120.8091

The results tabulated shows that geopolymers with PEG and H_2O_2 added have higher surface area compared to geopolymer without pore forming agent added which are 5.5525 m^2/g and 2.0646 m^2/g respectively. In more concise, adding PEG has resulted in higher surface area and higher pore volume whilst adding H_2O_2 has only increase the surface area while no big changes in pore volume. In case of pore size, smaller pore size is advantageous in adsorption because once the nitrogen molecules is adsorbed, it remains tightly bound in the pores (Mangun C. L. et al., 1997). Plus, the atomic radius size of Cu (II) ions is 1.45 Å. Hence, the Cu (II) ions is very much smaller than the pore size of the geopolymers.

Furthermore, as we observed through the isotherm linear plot in Figure 4.3, Figure 4.4 and Figure 4.5, their isotherm shows almost same shape which indicates that they are type IV isotherm and the materials are mesoporous. According to the

IUPAC (International Union of Pure and Applied Chemistry) classification, Na-geopolymer samples show type IV isotherms. The existence of hysteresis loops on adsorption/desorption isotherms of geopolymers indicate that it is mesoporous materials. The hysteresis loop originates from the difference in adsorption and desorption processes, which is attributed to the capillary condensation taking place in mesopores.

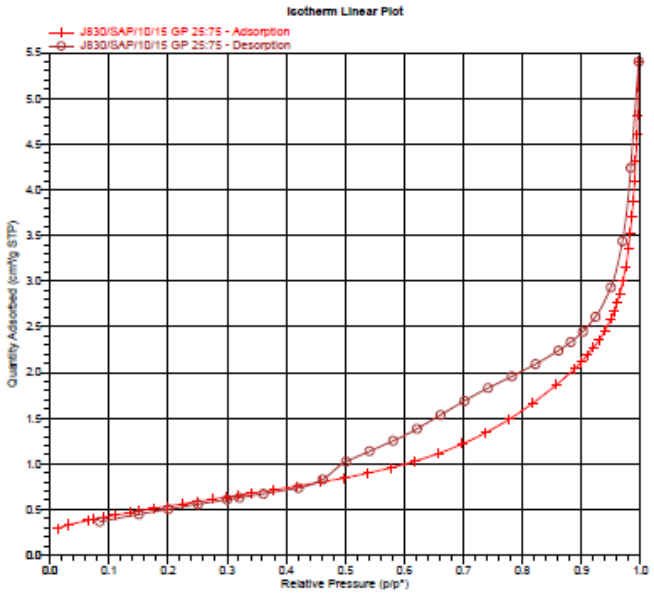

FIGURE 4.3 Isotherm linear plot for GP-0.75

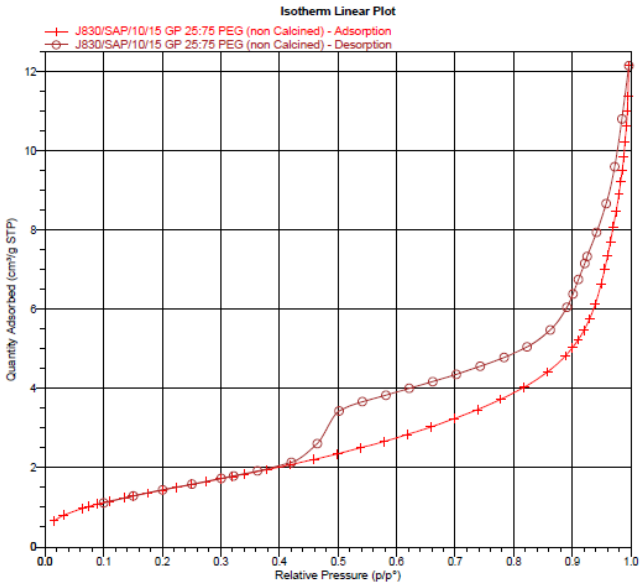

FIGURE 4.4 Isotherm linear plot for GP-0.75 PEG

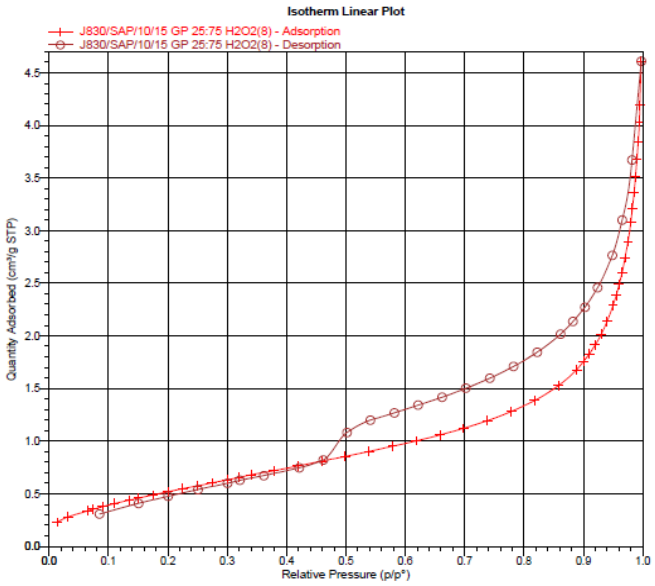

FIGURE 4.5 Isotherm linear plot for GP-0.75 H_2O_2

Another things is that it shows GP-0.75 PEG has relatively higher quantity adsorbed compared to GBFS based geopolymer and GP-0.75 H_2O_2. This proved that PEG is an effective pore forming agent that it increased the adsorption capacity by increasing the surface area and pore volume. However, the quantity of N_2 adsorbed by GP-H_2O_2 is less than the non-modified GP-0.75. From these, it can be concluded that GP-0.75 PEG has the most quantity adsorbed due to the high pore volume and surface area compared to other two geopolymers. Another important point that we can see is that the pore size is not the important element in adsorption, instead the pore volume and pore size which matter. This is why the quantity adsorbed by GP-0.75 and GP-0.75 H_2O_2 is nearly same eventhough their pore size has relatively much different.

In this case, the observation shows that H_2O_2 indeed can produced a foam geopolymers but the BET results show that it is not best applicable for adsorption. It also can be said that H_2O_2 acted as a physical blowing agent by creates trapping pockets of air (bubbles/tunnel of air) instead of pores as can be seen in Figure 4.6. It may not useful for adsorption purposes but it is very advance materials to be used in construction industry due to the light foam geopolymers concrete formed (Cilla M. S. et al, 2014; Posi P. et al., 2015).

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FIGURE 4.6 Images of GP-0.75 H_2O_2 surface

4.3.2 Particle Size Analysis (PSA)

PSA is a useful tool to determine the particle size of geopolymers. The size and shape of powders will affect the flow and compaction properties where a larger and more spherical particles will flow easier than smaller particles. However, smaller particles will dissolve more quickly and give higher suspension viscosities than larger ones. Besides, smaller particles with high surface charge (zeta potential) will typically improve suspension and emulsion stability. In case of adsorption, finer particles size of geopolymers will provide a good surface area and improve the efficiency of adsorption. This is supported with study by Krishna R H. et al. (2012) in which the study shows that at a fixed adsorbent dosage, the decrease in particle size increases the metal removal.

The result of PSA is presented in Figure 4.7, Figure 4.8 and Figure 4.9. GP-0.75 shows a mean particle size of 407.505 µm while GP-0.75 PEG shows a little bigger particle size, 468.700 µm. However, the changes is yet very small and it is expected will not affect the adsorption of copper so much. GP-0.75 H_2O_2 has the finest particle size that is 201.128 µm. This supposedly supported that GP-0.75 H_2O_2 has high potential for adsorption due to its very fine particle size. But, yet still from the BET results, it shows that GP-0.75 H_2O_2 has the least quantity adsorbed.

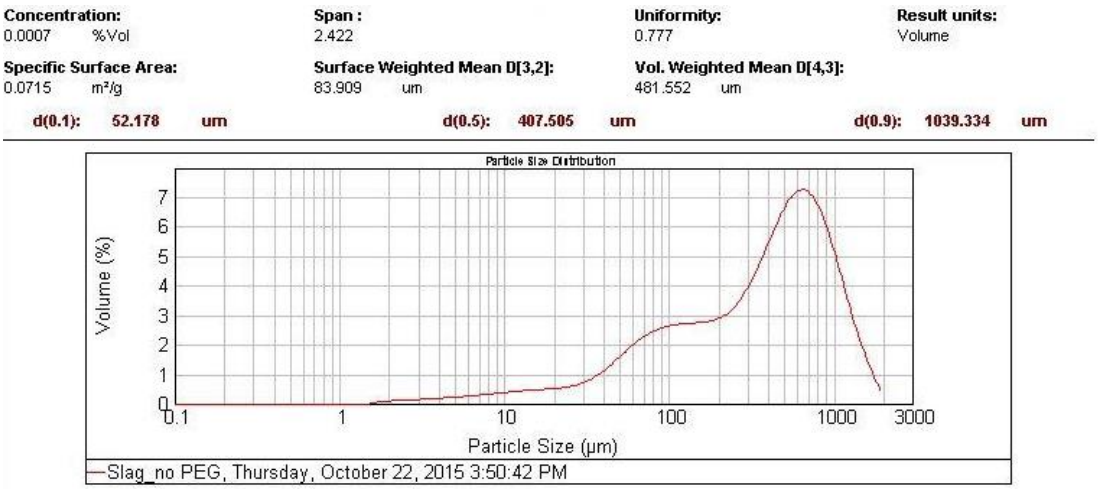


FIGURE 4.7 Particle size distribution curve of GP-0.75

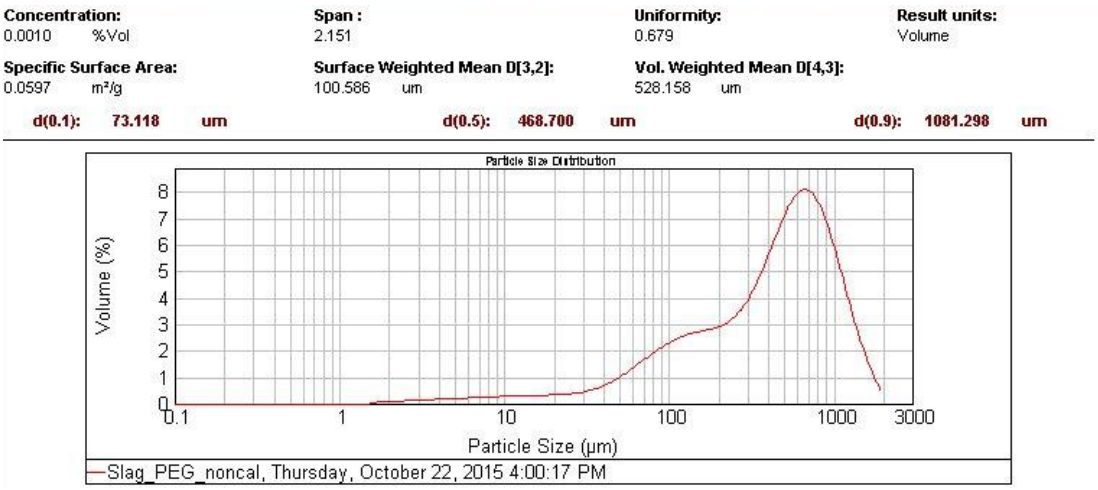


FIGURE 4.8 Particle size distribution curve of GP-0.75 PEG

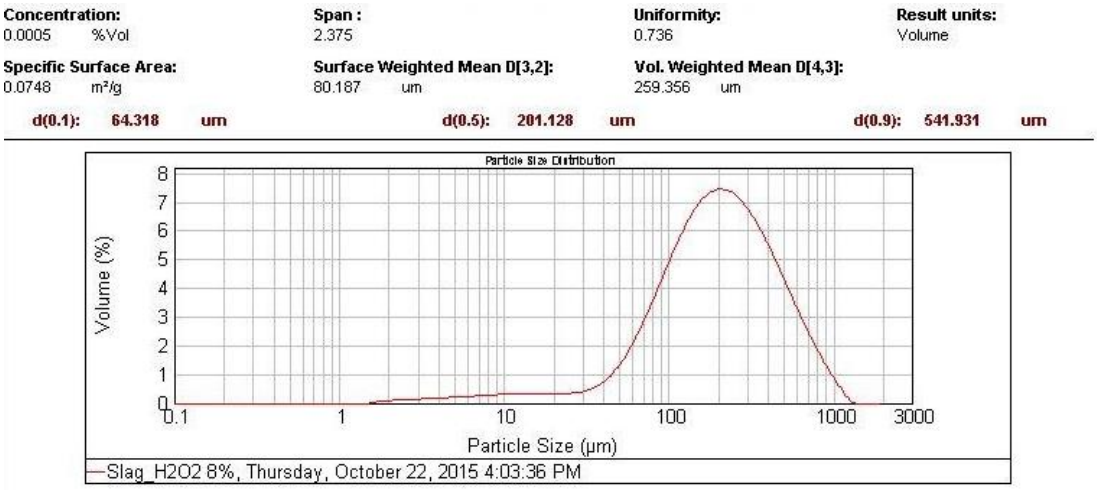


FIGURE 4.9 Particle size distribution curve of GP-0.75 H_2O_2

4.3.3 SEM analysis

All geopolymers were observed under PHOTOM machine at 500 magnification. Figure 4.10 shows the image of GBFS before geopolymerization while Figure 4.11 shows the images of geopolymers synthesized. The SEM images show the existence of pores on the geopolymers.

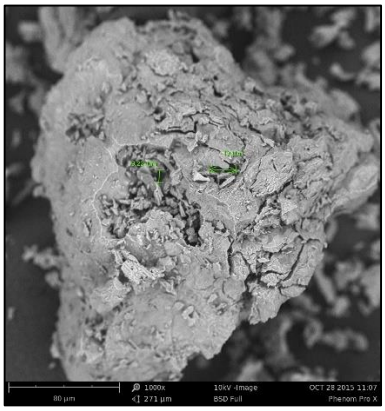


FIGURE 4.10 SEM images of GBFS before geopolymerization

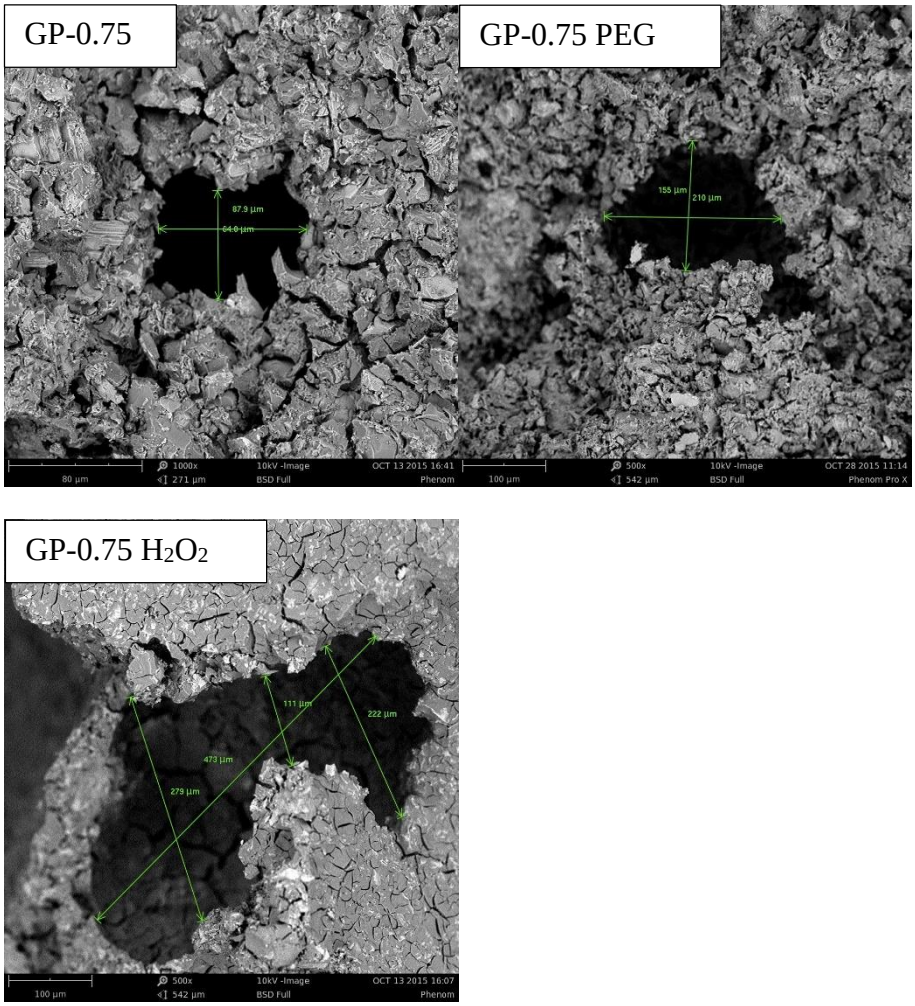


FIGURE 4.11 Slag based geopolymers before adsorption (500 x)

Furthermore, Figure 4.12 and Figure 4.13 shows the images of the synthesized geopolymers after the adsorption test. The EDX analysis also verify that there are copper ions on the used adsorbents (Figure 4.14).

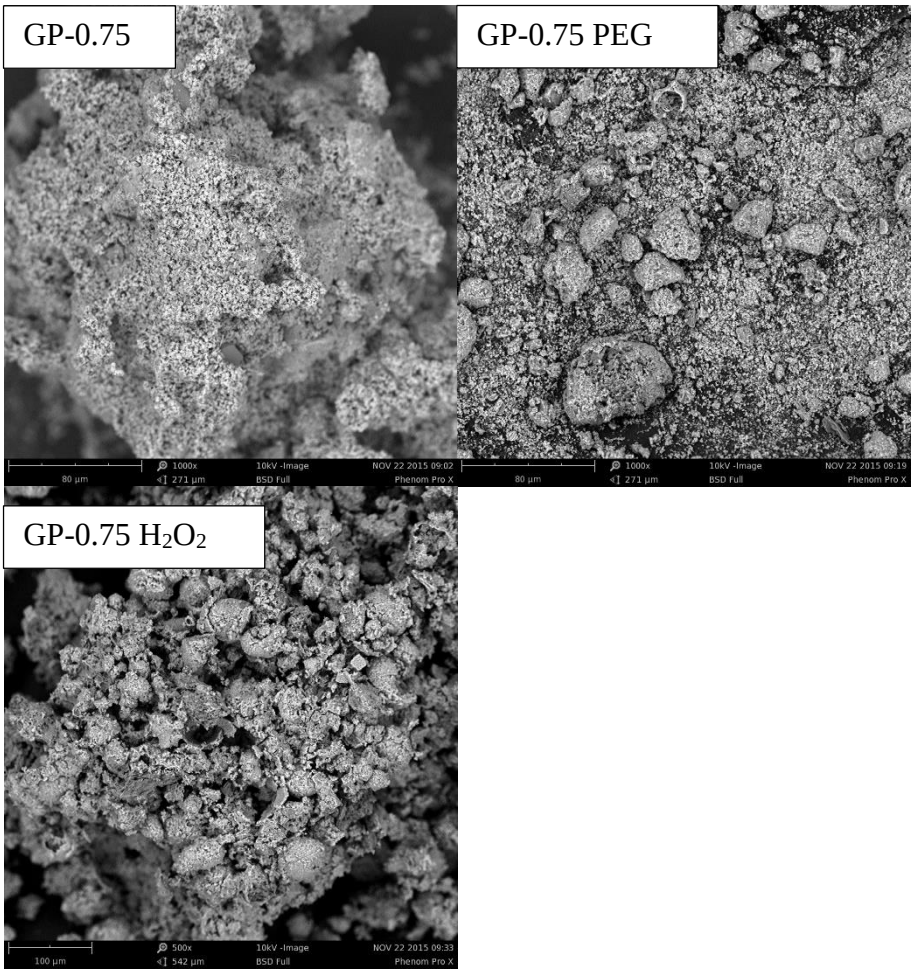
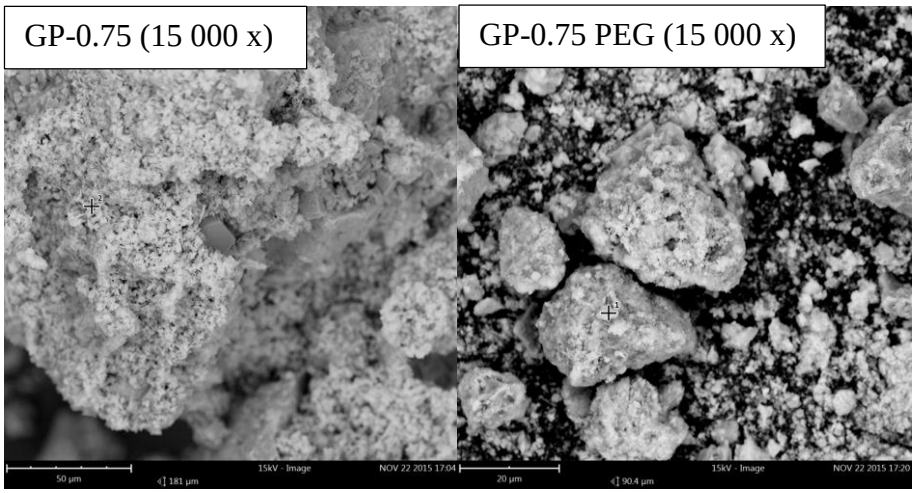


FIGURE 4.12 Slag based geopolymers after adsorption (1000 x)



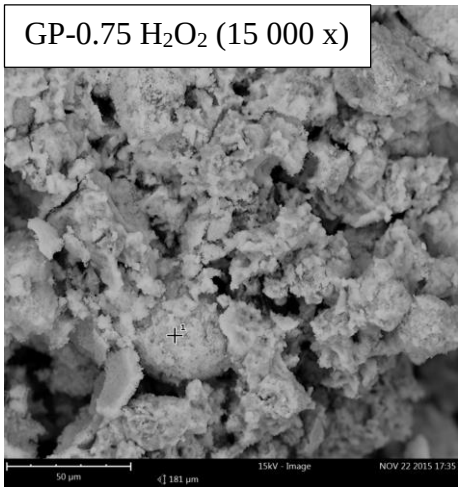


FIGURE 4.13 Slag baesd geopolymers after adsorption (15000 x)

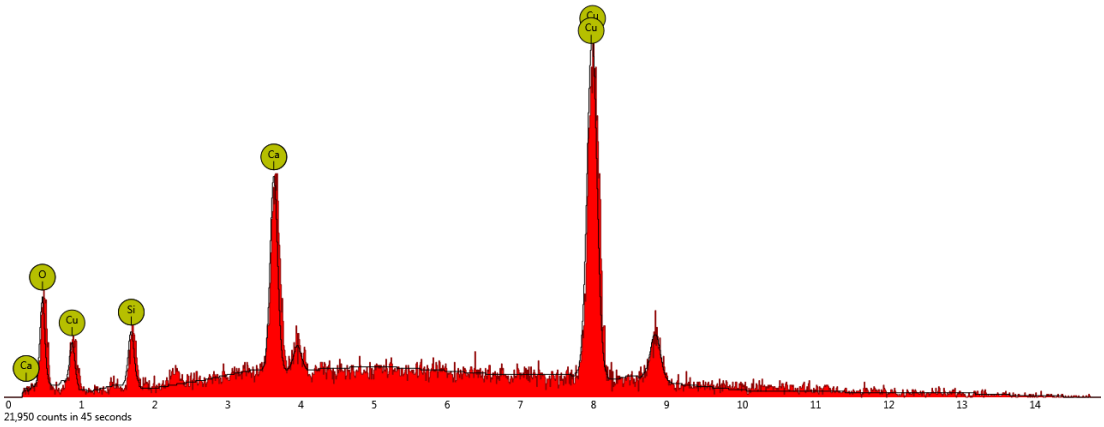


FIGURE 4.14 EDX analysis of GP-0.75 H_2O_2

4.3.4 TGA analysis

TGA run by measuring the weight loss with increasing temperature up to 800ºC with heating rate 10ºC/min. Figure 4.15 and Figure 4.16 show the TGA result of GP-0.75 PEG and GP-0.75 H_2O_2 respectively. Results show that up to 800ºC, about 11% weight loss in GP-0.75 PEG while for GP-0.75 H_2O_2 is about 16% weight loss. This is the proof that the geopolymers synthesized is very stable at high temperature. The sharp decrease before 200ºC is attributed to the loss of evaporable water in the geopolymer. After the initial rapid decline, the weight loss stabilized after 600ºC for GP-0.75 PEG and above 300ºC for GP-0.75 H_2O_2. This shows that

GP-0.75 H_2O_2 get stabilized faster at lower temperature than GP-0.75 PEG. This results were supported with study by Al Bakri A. M. M. et al. (2012) on fly ash based geopolymer. The fly ash based geopolymer also were stable at high temperature with only 11% weight loss.

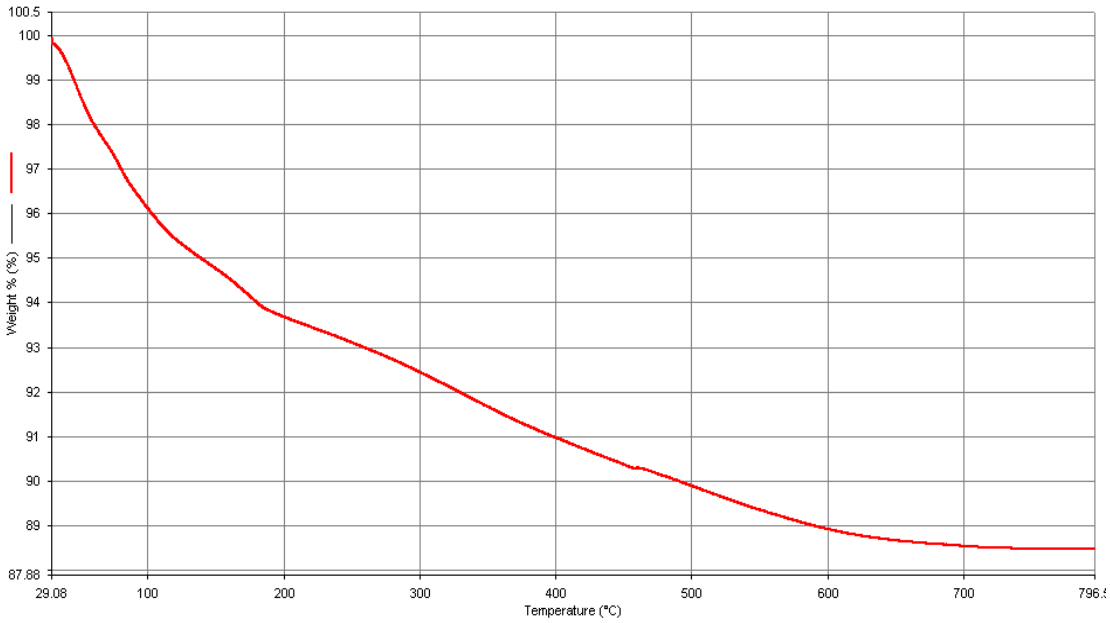


FIGURE 4.15 TGA curve for GP-0.75 PEG

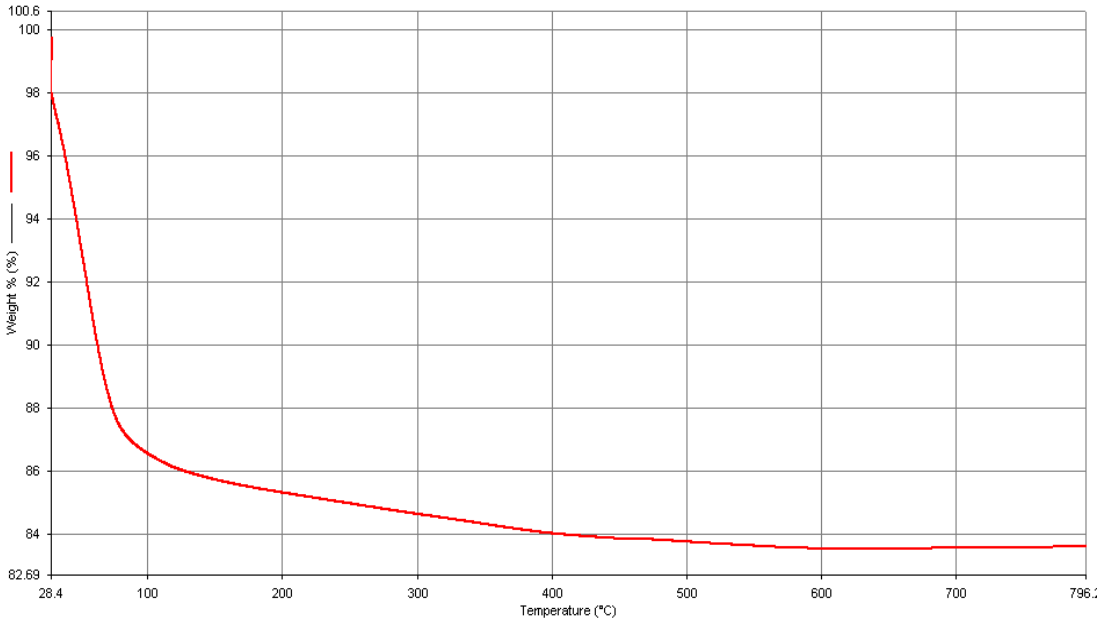


FIGURE 4.16 TGA curve for GP-0.75 H_2O_2

4.4 Standard Curve

Standard curve was developed initially as reference for adsorption test later on. The standard curve was plotted using 5, 10, 15, 20, 25 and 30 ppm as shown in Table 4.5. This standard curve will be author reference in the whole adsorption test. Based on this standard curve (Figure 4.17), the author can determine the final copper concentration by measuring the intensity change.

TABLE 4.5 Intensity vs. concentration of copper

Sample	Intensity	Concentration (mg/L)
Blank	0	0
Standard 5ppm	515031.33	5
Standard 10ppm	1220004.54	10
Standard 15ppm	1835309.89	15
Standard 20ppm	2498413.7	20
Standard 25ppm	3143548.79	25
Standard 30ppm	3726936.17	30

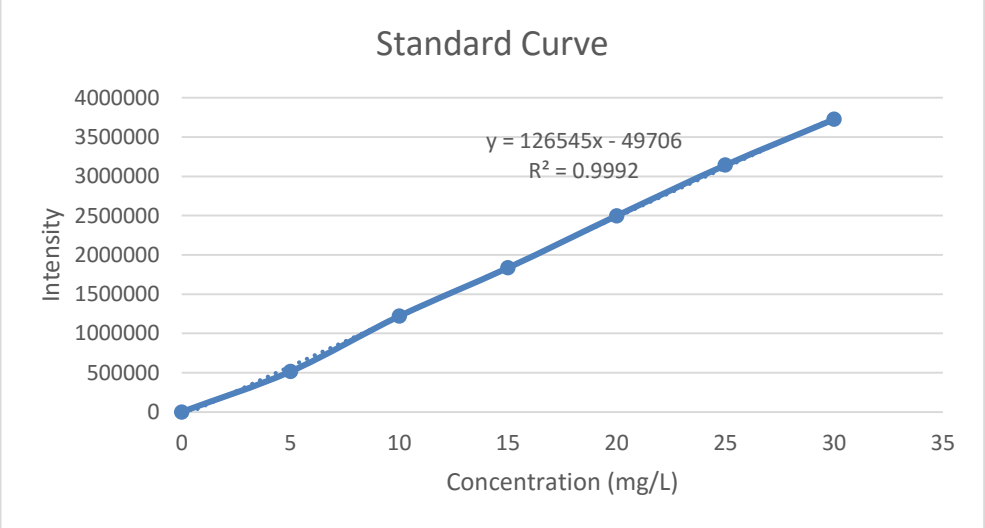


FIGURE 4.17 Standard curve of adsorption test

4.5 Adsorption Test

Adsorption test had been carried out using copper sulphate ($Cu_2SO_4.5H_2O$) solution to determine the adsorption ability of the geopolymers. The effect of initial adsorbent dosage, contact time and pH has been carried out to observe the effect of these parameters to adsorption.

4.5.1 Effect of initial adsorbent dosage

The adsorption process has been carried out using 100 ml of 50 ppm copper sulphate solution. Different amount of adsorbent was added at neutral pH of copper sulphate solution with contacting time of 3 hours at 25°C.

The percentage removal of copper is calculated by using Equation 9. From Figure 4.18 it has been found that adsorption increases with adsorbent dose and then remains constant after certain dose of adsorbent. As the amount of adsorbent increases, the adsorption sites also increase until all the sites are fully filled where that means it reach the maximum (equilibrium capacity).

$$Percentage\ removal = \frac{Co - Ct}{Co} \times 100\% \quad (9)$$

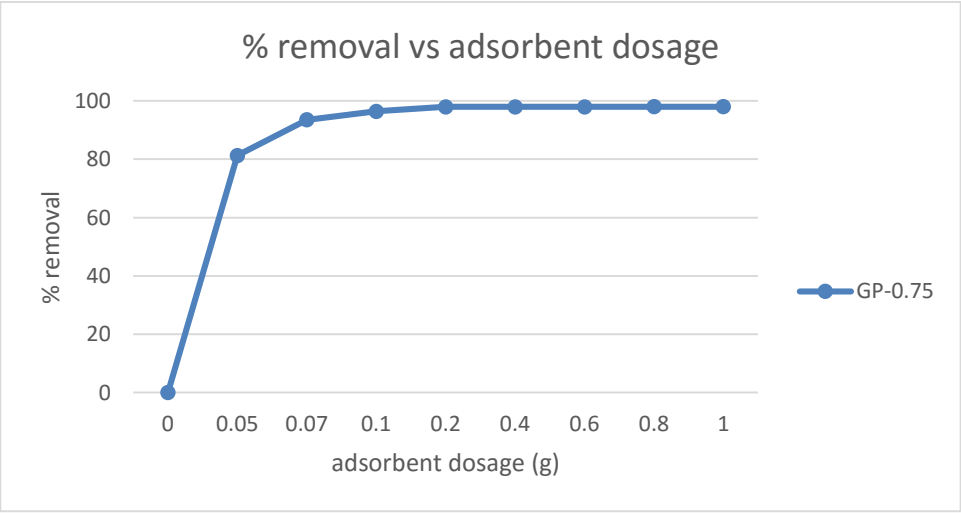


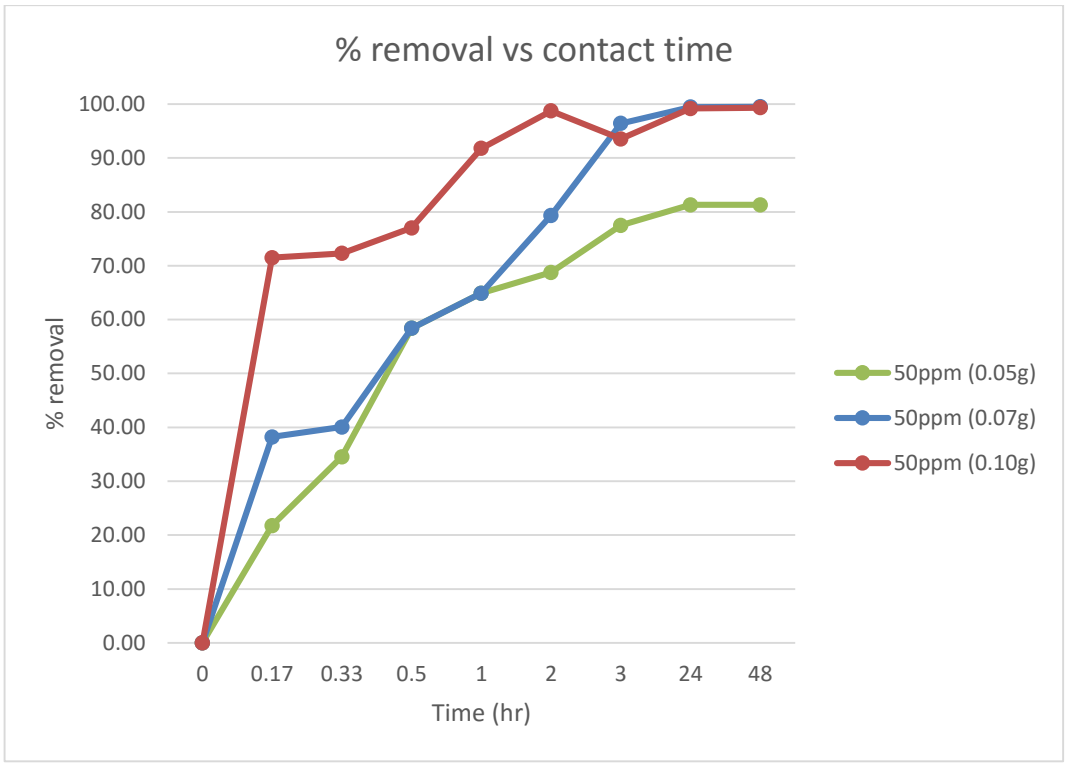
FIGURE 4.18 Effect of initial adsorbent dosage on adsorption of copper

The result shows that 0.1 g of adsorbent are able to achieve up to 96% removal of copper compared to when 0.05 g adsorbent being used, the percentage removal only up to 81%. Besides, almost all copper were successfully removed for 50 ppm initial concentration of copper by using 0.2 g and above dosage of adsorbent. The increase in adsorption with the adsorbent dosage can be attributed to the availability of greater surface area and larger number of adsorption sites (Gulipalli C. S. et al., 2011).

4.5.2 Effect of contact time

Contact time is also a significant factor in affecting the adsorption activity by geopolymers. It also would be useful in determine the equilibrium time for the kinetic and isotherm study. Various mass of adsorbents have been added to 100 mL of 50 ppm of Cu (II) solutions and the concentration is measured every preselected time. The results are shown in Figure 4.19. It shows that as time increase, the copper ions is continually adsorbed until all is removed (if it reached 100% removal) while if it is less, means that it has reached the maximum adsorption capacity for the respective amount of adsorbent. Moreover, it shows that GP-0.75 is fully saturated at 80% removal for 0.05 g adsorbents after 3 hours contact time. Hence, to remove 100% of copper from 100 ml of 50 ppm Cu (II) solutions, the dosage has to be more than 0.05 g.

The adsorption of copper also remains almost constant and the difference between the adsorptive uptake at 3 hours and 24 hours and is less than 2% of that at 48 hours. Therefore, a steady-state approximation was assumed and a quasi-equilibrium situation is considered at t=3 hours. pH was not adjusted in this experiments. Based on these results, pseudo first order kinetic studies and pseudo second order kinetic studies are performed for all geopolymers.



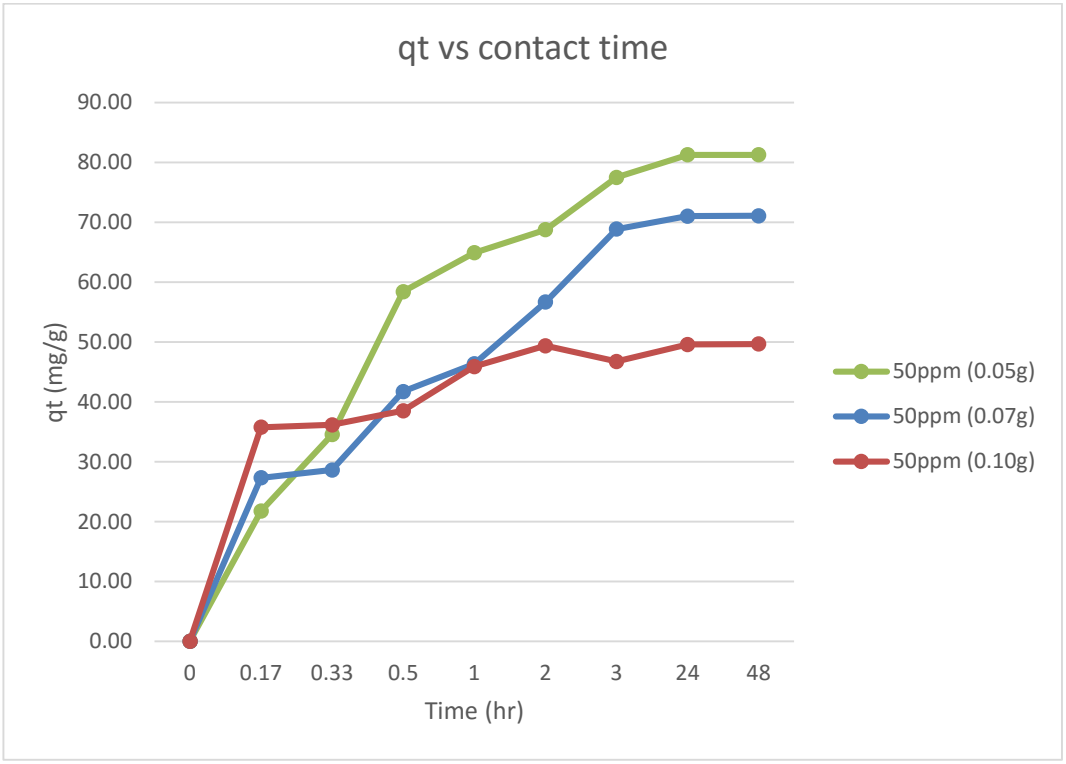


FIGURE 4.19 Effect of contact time on copper adsorption using GP-0.75

4.5.3 Effect of pH

A blank solution containing 100 ml of 50 ppm Cu (II) solution and adsorbent was prepared with different pH values of 2, 4, 6, 7, 8 and 10, respectively by adjusting 0.1 M HCl and 0.1 M NaOH. A constant amount of 0.10 g of GP-0.75 adsorbents was contacted for 3 hours.

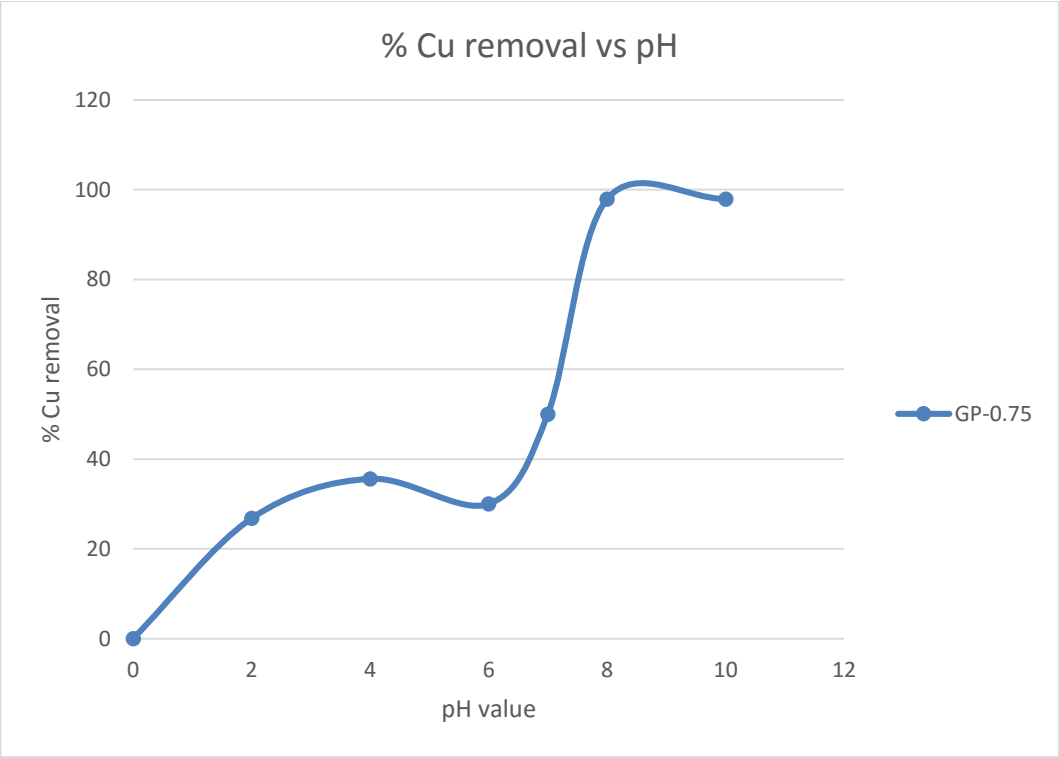


FIGURE 4.20 Effect of pH on copper adsorption using GP-0.75

Figure 4.20 shows that the percentage removal of copper increases as the pH increases and the percentage removal is maximum at pH 8. The percentage removal is up to 97.9% as the pH reached 8. A sudden increase in copper removal is expected due to the precipitation of copper hydroxide ($Cu(OH)_2$) when sodium hydroxide (NaOH) is added initially to increase the solution pH. Besides, in acidic solution, the adsorption is small due to H^+ ions that have to compete strongly with Cu^{2+} ions for active sites (Ge Y. et al., 2015).

4.5.4 Kinetic study of adsorption

The kinetic study of GP-0.75, GP-0.75 PEG and GP-0.75 H_2O_2 adsorption capabilities was observed by conducting the adsorption test at various initial concentration of Cu (II) solution and a sample extraction at 10, 20, 30, 60, 90, 120 and 240 minutes. Pseudo first order and second order equations are applied to determine the kinetic of adsorption activity for the geopolymers.

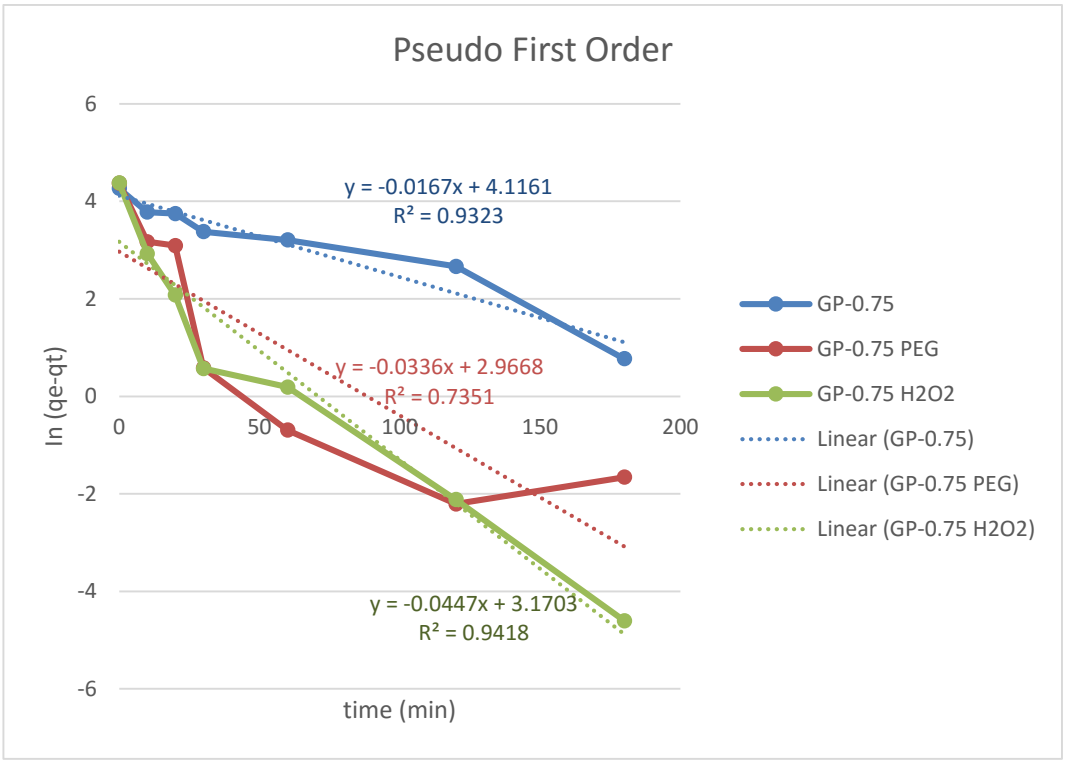


FIGURE 4.21 Pseudo First Order studies

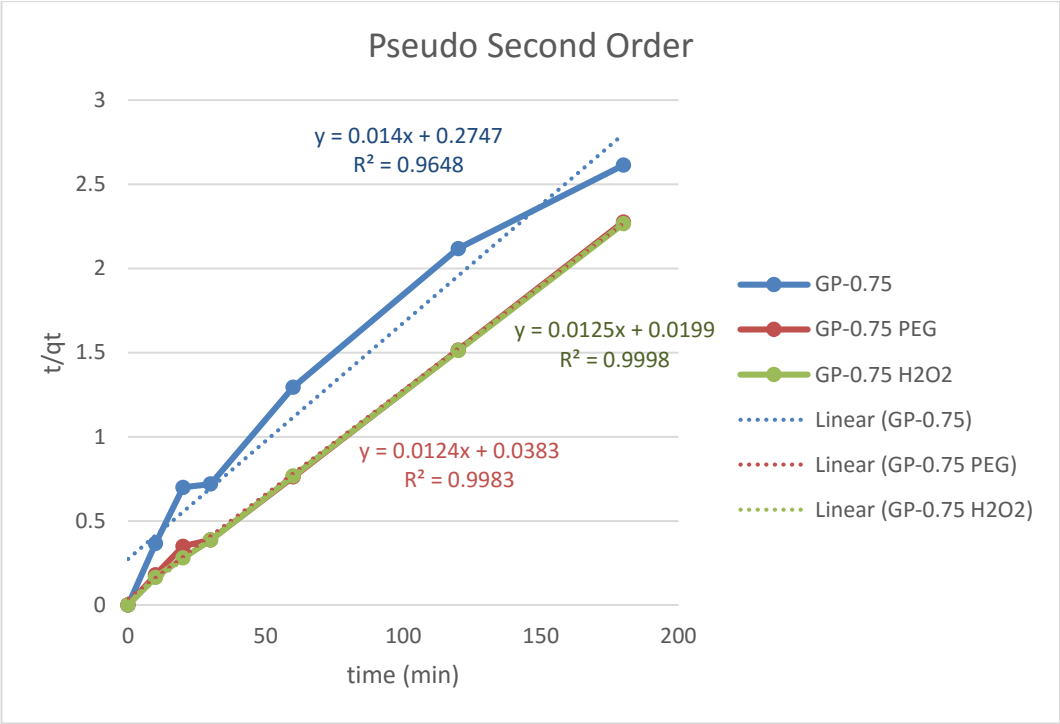


FIGURE 4.22 Pseudo Second Order studies

The values of the pseudo-first-order adsorption rate constant k_1 are determined using Equation 10 by plotting log (q_e - q_t) against t for copper adsorption onto all the adsorbents with C_o=50 ppm at 298 K for the first 3 hours.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (10)$$

The graph of pseudo second order then was plotted by using Equation 11 where k_2 can be determined. q_t is the amount adsorbed (mg/g) at time t and the amount adsorbed at equilibrium, q_e is determined using Equation 12.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \qquad (11)$$

$$q_e = \frac{C_i - C_e}{M} V \qquad (12)$$

Where,

k_1=rate constant for pseudo first order rate

k_2=rate constant for pseudo second order rate

C_i=initial adsorbate concentration, ppm

C_e= equilibrium adsorbate concentration, ppm

V=solution volume, L

M=adsorbent mass, g

The values of constant k_1, k_2 and q_e for both pseudo first and second order is determined respected to the graph (Figure 4.21 and Figure 4.22) and is tabulated in Table 4.6 and 4.7.

TABLE 4.6 Values for pseudo first order studies

1st order	slope	intercept	R^2	k_1	q_e
GP-0.75	-0.4732	5.0081	0.9323	-1.08978	71.03
GP-0.75 PEG	-1.1658	5.6139	0.7351	-2.68484	79.3
GP-0.75 H_2O_2	-1.3902	6.0492	0.9418	-3.20163	79.46

TABLE 4.7 Values for pseudo second order studies

2nd order	slope	intercept	R^2	k_2	q_e
GP-0.75	0.4264	-0.5898	0.9648	-0.02387	71.03
GP-0.75 PEG	0.3539	-0.6343	0.9983	-0.01988	79.3
GP-0.75 H_2O_2	0.3564	-0.6577	0.9998	-0.01913	79.46

The results show that the adsorption activities for all geopolymers fitted the pseudo-second order kinetic model. This kinetics is important during the designing of treatment plants where it tells the solute uptake rate and residence time controls of sorbate uptake at the solid-solution interface.

4.5.5 Isotherm study of adsorption

Isotherm study was conducted using the same experimental data obtained from the kinetic studies experiment. The studies of isotherm of the geopolymers have

been tested for Langmuir and Freundlich isotherm. The plotted graph (Figure 4.23 and Figure 4.24) are based on the correlation from Equation 13 to Equation 14 where Equation 13 show the relationship between q_e and C_e for Langmuir isotherm.

$$\frac{1}{q_e} = \frac{1}{q_m K_l}\frac{1}{C_e} + \frac{1}{q_m} \quad (13)$$

Where,

q_m= maximum adsorbates on the adsorbent, mg/g

K_l=Langmuir constant of adsorption, L/mg

While for Freundlich isotherm, the relationship between q_e and C_e can be represented using correlation in Equation 14.

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (14)$$

Where,

K_f=indicators of adsorption capacity

n=adsorption intensity

Figure 4.23 and figure 4.24 show the Langmuir and Freundlich isotherms plotted respectively for all the geopolymers.

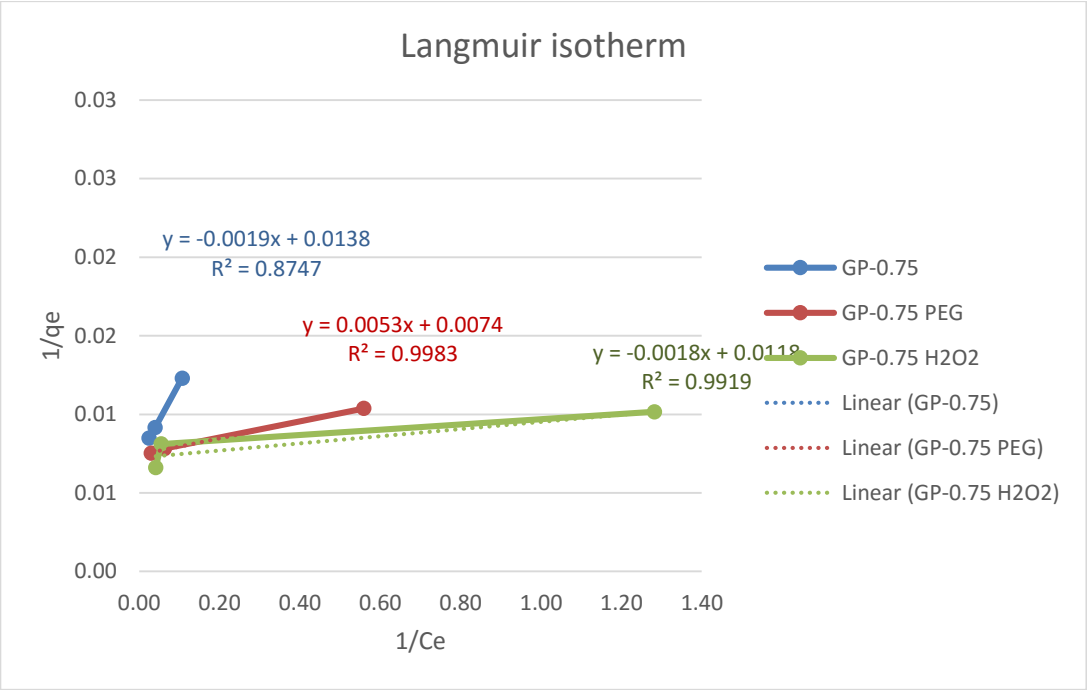


FIGURE 4.23 Langmuir isotherm studies

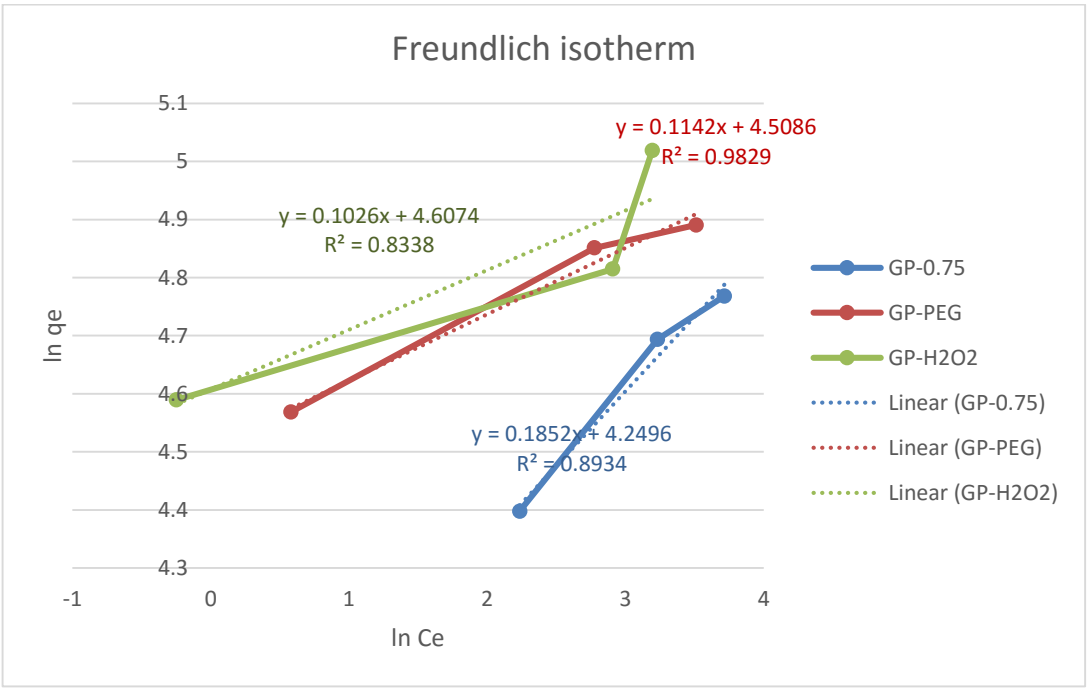


FIGURE 4.24 Freundlich isotherm studies

TABLE 4.8 Values for Langmuir isotherm studies

Langmuir	slope	intercept	q_m (mg/g)	k_1	R^2
GP-0.75	-0.0019	0.0138	72.463768	-0.00002622	0.8747
GP-0.75 PEG	0.0053	0.0074	135.13514	0.00003922	0.9983
GP-0.75 H_2O_2	-0.0018	0.0116	86.206897	-0.00002088	0.9919

TABLE 4.9 Values for Freundlich isotherm studies

Freundlich	slope	intercept	n	K_f	R^2
GP-0.75	0.1852	4.2496	5.399568	70.07737579	0.8934
GP-0.75 PEG	0.1142	4.5086	8.7565674	90.79461703	0.9829
GP-0.75 H2O2	0.1026	4.6074	9.7465887	100.2232302	0.8338

The best fitted for the isotherm studies will be determined by the highest R^2 value. Results obtained show the isotherm studies of GP-0.75 fitted well into Freundlich isotherm whereas for GP-0.75 PEG and GP-0.75 H_2O_2 fitted well into Langmuir due to high correlation factor, R^2 observed.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The GBFS based geopolymers with high porosity has been successfully synthesized by mixing method. From the five geopolymers synthesized without pore forming agent, GP-0.75 is the optimum silica ratio due to the porosity volume.

As for another study which is by modifying GP-0.75 with 3% of poly-ethylene glycol (PEG) during mixing, it can be concluded that GP-0.75 PEG exhibits better adsorbent properties as compared to GP-0.75. Another study is by modifying GP-0.75 with 8% of hydrogen peroxide (H_2O_2) and it also exhibits better adsorbent properties than GP-0.75. Moreover, the modified geopolymers with pore forming agent exhibit more pore volume and higher surface area compared to the non-modified GBFS based geopolymers.

In the adsorption test, the adsorption activities of the GBFS based geopolymer is favourable at high alkaline condition in which the optimum pH for GBFS based geopolymer is pH 8. Besides, the adsorption activities also increase with increase in adsorbent dosage and high contact time until it achieve equilibrium. For kinetic studies, all geopolymers synthesized fitted pseudo second order kinetic models with R^2=0.9648 for GP-0.75 while for GP-0.75 PEG and GP-0.75 H_2O_2 with R^2=0.9983 and R^2=0.9998 respectively. So forth, GP-0.75 fitted well in Freundlich isotherm with R^2=0.8934 while GP-0.75 PEG and GP-0.75 H_2O_2 fitted well in Langmuir isotherm with R^2=0.9983 and R^2=0.9919 respectively for the isotherm equilibrium study.

This project has successfully proven the adsorption capabilities of GBFS based geopolymers and it was clearly proven that the existence of pore forming agent produces better adsorbent type of GBFS based geopolymers.

5.2 Recommendation

For future works, it is suggested to investigate the effect of adding pore forming agent, hydrogen peroxide in modifying the geopolymer to the copper removal in the properties of chemical precipitation process instead of adsorption. This is arguable due to the high percentage removal using GP-0.75 H_2O_2 even though it has less pore volume.

Other than that, the adding of pore forming agent, poly-ethylene glycol in modifying the geopolymers could be studied with other based of geopolymers such as metakaolin and fly ash. It may has better adsorption capabilities than GBFS based geopolymers. Besides, desorption test also should be conducted to investigate the practicality of the geopolymers as adsorbents.

Furthermore, impressive results shown by GBFS based geopolymers in copper removal should be a benchmark to use them for removing other types of heavy metals. Apart from that, further study also can be done by modifying them using other pore forming agent to fit the purpose of effectively removing heavy metals via adsorption. Lastly, it is recommended to test the geopolymers synthesized in a real waste water sample that contains heavy metals to see the impracticality of the adsorbents in the industrial industries.

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